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TECHNICAL PAPER No. 5

SURVEY OF THE RIVER TEES

Part II.—The Estuary—Chemical and Biological

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Ordnance Survey 1931.

The Altitudes and Contours are given in Feet above Ordnance Survey Datum. (Mean Sea Level.)



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SURVEY OF THE RIVER TEES

Part II.—The Estuary—Chemical and Biological

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## PREFACE

**D**URING recent years there has been a growing appreciation of the need for research on the application of practicable methods and the scientific development of new methods of avoiding or reducing the pollution of the rivers and other water supplies of the country by industrial effluents and sewage. To meet this need the Water Pollution Research Board was set up in June, 1927, to submit schemes for research on the various problems involved and to supervise approved investigations.

One of the first conclusions reached by the Board was that reliable information was urgently required as to the effects on rivers of various polluting discharges, and the Board recommended that a comprehensive scientific survey of a typical river flowing largely through an industrial area should be undertaken. It was known that rivers which had received polluting liquids were capable of self-purification under certain conditions, but there was a lack of exact knowledge regarding those conditions and the quantities of various effluents which could be allowed to enter a river without causing serious pollution and unduly retarding the processes of self-purification.

It was decided that the River Tees afforded the main characteristics desirable in a pioneer investigation of this kind. Further, the work that had previously been carried out on the Tees, although insufficient to provide answers to the questions involved, was sufficient to enable a programme of research to be fairly clearly mapped out. Preliminary enquiries had also indicated that local interests would be willing to afford facilities and to co-operate in any Consultative Committee set up. A River Tees Survey Committee of the Board was accordingly appointed to draw up a detailed programme of investigation and to supervise the work, and on the recommendation of the Board the Department also set up a River Tees Survey Consultative Committee representative of the various local interests, for the purpose of ensuring effective consultation with those who had offered their co-operation.

The work of the survey, which occupied four years from April, 1929, to April, 1933, was divided into two main sections, comprising the tidal and non-tidal reaches respectively, and the work on the tidal reach was further sub-divided into two sections, the one to secure hydrographical data and the other to obtain chemical and biological information. For the hydrographical measurements a hydrographical surveyor was appointed and the work was carried out in close co-operation with Vice-Admiral Sir H. Percy Douglas, K.C.B., C.M.G., a member of the Survey Committee, who was then Hydrographer of the Navy. The results of the hydrographical part of the survey, which was completed during the first two years, are described in Water Pollution Research Technical Paper No. 2 published in 1931. In connection with the chemical and biological survey of the non-tidal reach, which was undertaken for the Department by the Ministry of Agriculture and Fisheries, a fixed laboratory was equipped at Barnard Castle and a travelling laboratory was used for those observations which had to be made on the spot and without delay. It is anticipated that a technical paper describing the survey of the non-tidal reach will be published shortly.

The chemical and biological survey of the tidal reach described in this report—Technical Paper No. 5—was carried out for the Department by the Marine Biological Association of the United Kingdom under the direction of Dr. E. J. Allen, C.B.E., D.Sc., F.R.S., by the courtesy of the Council of the Association. For this part of the work a laboratory was equipped at the Cleveland Shipyard, Middlesbrough, where accommodation was obtained through the kindness of the late the Hon. Sir Charles A. Parsons and Messrs. The Parsons Marine Steam Turbine Company, Ltd., a motor launch and a dinghy were also obtained and used throughout the survey of the tidal reach.

Mr. W. B. Alexander, M.A., who was in local charge of the work on the tidal reach from the beginning of the survey until September, 1930, was responsible for the biological observations and experiments during that period, Dr. B. A. Southgate was responsible for the chemical work throughout the survey and was in local charge from October, 1930, to April, 1933, and Mr. R. Bassindale, M.Sc., was responsible for the biological work from October, 1930, to April, 1933. Mr. W. H. Jackson and Mr. J. Moor assisted throughout the survey in the



collection and chemical examination of samples. Close co-operation was maintained with the scientific staff, Dr. R. W. Butcher, Dr. J. Longwell and Mr. F. T. K. Pentelow, B.A., engaged on the survey of the non-tidal reach of the river under Dr. E. S. Russell, O.B.E., Director of Fishery Investigations of the Ministry of Agriculture and Fisheries. Mr. Pentelow took part in the work on the migration of smolts during the spring of 1931 described in Chapter XIV and in part of the work described in Chapters XI and XIII. This report was drafted by Dr. Southgate and Mr. Bassindale under the direction of Dr. E. J. Allen and Mr. H. W. Harvey, M.A., of the Marine Biological Association; Mr. Harvey also gave much valuable advice and assistance in the work of the survey.

Special reference must be made to the valuable advice and guidance received from the late Professor G. C. Bourne, D.Sc., F.R.S., who was a member of the Water Pollution Research Board and Chairman of the River Tees Survey Committee until his death in March, 1933, and from the late Mr. J. H. Amos, who was General Manager of the Tees Conservancy Commission until 1931 and was Chairman of the River Tees Survey Consultative Committee.

In addition to the acknowledgments already made, the Department wishes to express appreciation of the valuable assistance rendered by the various local authorities, other organisations, industrial undertakings and individuals in the Tees area. The Tees Conservancy Commission, their General Manager, Mr. F. T. Natrass, their Engineer, Mr. P. A. R. Leith, and their Harbour Master and staff aided the work by allowing the use of records and data in their possession, and on several occasions provided men and boats and assistance in the preparation of diagrams. Local Authorities supplied data relating to sewers and the quantities of sewage discharged and provided facilities for the collection of samples. All the local firms approached supplied information relating to their industrial effluents and allowed the collection of samples. The following firms and members of their staffs were particularly helpful in the work relating to coke oven effluents: Messrs. Dorman, Long and Co., Ltd., and Dr. J. A. Roelofsen, Mr. H. E. Wright and Mr. T. Biddulph Smith; I.C.I. (Fertilizer and Synthetic Products, Ltd.) and Dr. R. E. Slade, Mr. M. P. Appleby and Dr. Tyrer; and The Cargo Fleet Iron Works and Mr. Caddick. The Tees Fishery Board gave permission for the netting and marking of salmon and sea trout smolts and The Tees Valley Water Board and their Engineer, Mr. G. R. Collinson, M.Inst.C.E., assisted in the provision of water to the laboratory and in other directions. Many landowners and farmers allowed access through their estates to various points along the river.

During the course of the investigation surveys of the Firth of Tay and of the Estuary of the Tyne were made with the object of obtaining data of value in aiding in the interpretation of the results of the survey of the Tees. In this work valuable advice and assistance were provided by Professor A. D. Peacock of Dundee, The Tay Salmon Fishery Company, Ltd., Professor A. Meek of Armstrong College, Newcastle-upon-Tyne, and Dr. H. O. Bull of the Marine Laboratory at Cullercoats.

The Department also desires to acknowledge the assistance given by the Scottish Fishery Board and their Inspector of Salmon Fisheries, Mr. W. J. M. Menzies, F.R.S.E., in examining the scales of salmon and sea trout and in examining trout for furunculosis, by The British Museum (Natural History) in identifying specimens and by the Meteorological Office of the Air Ministry in furnishing data of the rainfall in the water-shed of the Tees throughout the period of the survey.

H. T. CALVERT,

*Director of Water Pollution Research.*

DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH,

16 Old Queen Street,

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September, 1935.



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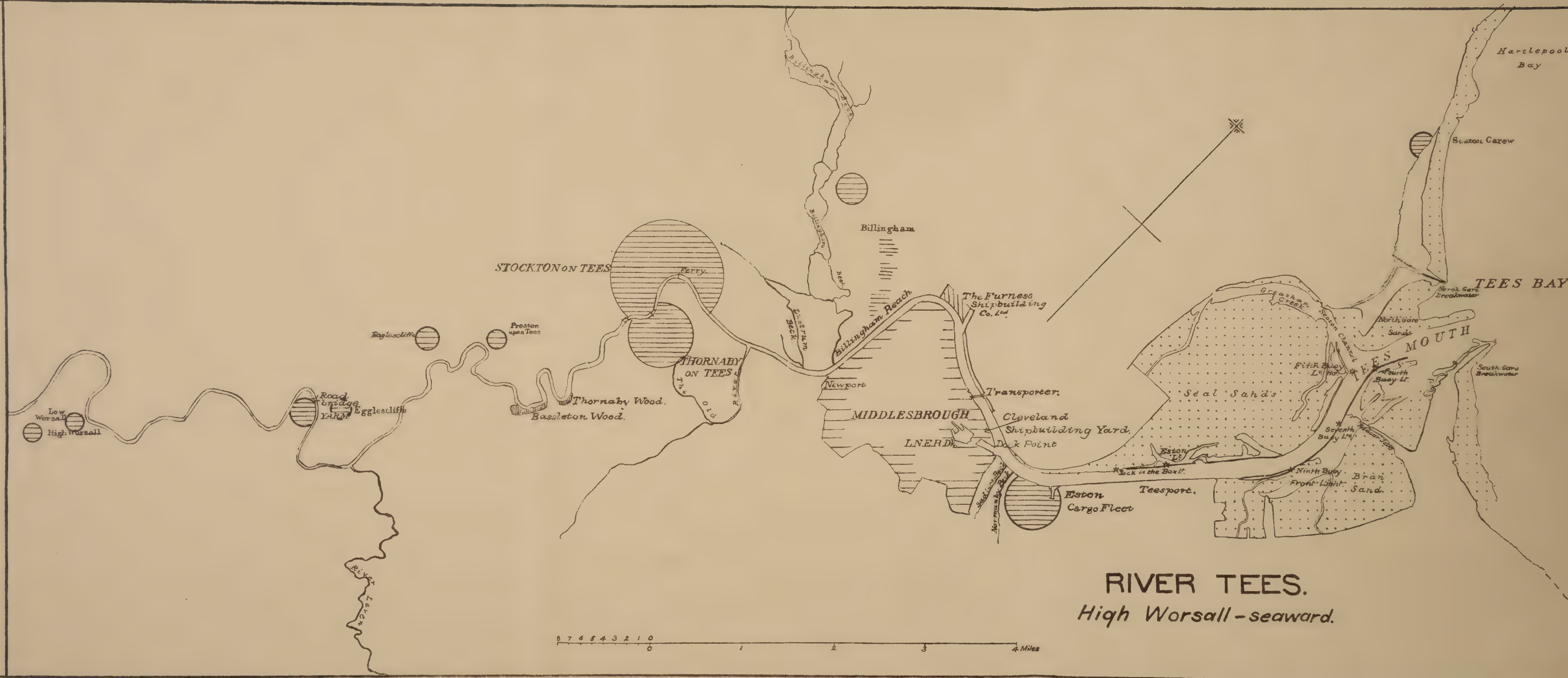


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RIVER TEES.  
High Worsall-seaward.



# FINAL REPORT ON THE SURVEY OF THE RIVER TEES

## Part II :—The Estuary—Chemical and Biological

### CHAPTER I

#### GENERAL INTRODUCTION AND SUMMARY

THE tidal section of the River Tees extends from the sea to High Worsall, a distance of 25 miles. From Yarm to Stockton the river runs between natural banks through country largely agricultural in character; the channel is not dredged and is little used by shipping. At low water throughout this stretch the water is fresh but at high springs salt water travels to within one or two miles of Yarm. Below Stockton the Estuary passes through a thickly populated industrial area and the channel, which is navigable, is dredged to ensure a minimum depth of about 12 ft. at low water. In the stretch of about 7 miles from Stockton to Cargo Fleet numerous industrial effluents and untreated sewage from a population of about 280,000 are discharged. As a result, large numbers of migratory fish passing through the Estuary are killed each year, especially in the spring, and the value of the salmon and sea trout fishery, which was formerly considerable, has greatly declined.

The main objects of the investigation of the Estuary were to study the varying physical and chemical conditions and the types and distribution of animal and plant life, with special reference to the effects of discharges of sewage and industrial wastes. Such a survey necessarily involved the accumulation and examination of a large collection of observational and experimental data, which will be dealt with in greater detail in subsequent chapters. In this chapter a general outline is given of the main lines and results of the survey.

The whole body of water in the Estuary moves up and down with each flood and ebb of the tide. Superimposed on this movement, the fresh water entering the Estuary from the upper river flows to the sea mainly in the surface layers, picking up and carrying with it salt water from beneath. To take the place of the latter there is a residual movement of salt water from the sea up the Estuary in the bottom layers. As a result of this circulatory system the water in the middle stretch of the Estuary is stratified, the salinity increasing from the surface to the bottom. Matter suspended or dissolved in the surface layers moves further seaward on the ebb than upstream on the flood and thus passes gradually out to sea. On the other hand, matter remaining suspended in the bottom layers moves further up-stream on the flood than it moves seaward on the ebb. In times of strong fresh-water flow from the upper river the degree of stratification is greatly increased, and after heavy rains it is possible at certain positions to have nearly fresh water at the surface and almost undiluted sea water at the bottom.

Water entering the tidal reaches moves relatively slowly seawards, especially if the volume of fresh water coming in from the upper river is small. The mean time taken for all layers of a body of water to travel through the Estuary has been estimated to vary from about 6 days under dry weather conditions to about  $2\frac{1}{2}$  days under average winter conditions. Substances carried in the upper layers will reach the sea more rapidly and substances in the deeper layers less rapidly than the calculated mean times.

As a result of the decomposition of sewage and industrial effluents, brought about largely through the agency of bacteria, the water in the central part of the Estuary is partially de-oxygenated. The extent of the oxygen deficiency depends mainly on the temperature, the growth and activity of bacteria increasing greatly as the water becomes warmer, and during hot summer months the concentration of dissolved oxygen may fall as low as 5 per cent. of the saturation value. The temperature of the Estuary water is, in fact, usually slightly higher than that of the upper river water or of the sea, as very large quantities are used by industrial plants in condensers and coolers and are returned to the Estuary at a higher temperature.



The bed of the tidal reach above Stockton consists mainly of gravel, rock, and clay; below Stockton the clay is gradually replaced by soft mud over a distance of about 6 miles, and this is in turn replaced by clean sand extending to the open sea. It is possible that the soft glutinous muds in the central stretch are partly the result of the deposition of substances discharged from sewage and industrial outfalls.

At the mouth of the Estuary the marine fauna and flora are varied and abundant; near Yarm fresh water animals and plants are very numerous; in the central portion of the Estuary there is little variety or abundance of either marine or fresh water organisms and at Newport, 2 to 3 miles below Stockton, only a few species of animals and plants survive. The region containing the minimum numbers of species is, in the Tees, coincident with the region of maximum pollution. In the unpolluted sandy Estuary of the Tay, however, there is a similar dearth of species in the central reaches, although marine animals penetrate into rather less saline water than in the Tees. Similarly, in the muddy Estuary of the Tamar, the marine fauna, whilst progressively reduced as the head of the Estuary is approached, does not die out quite so quickly as in the Tees. In all three estuaries it is evident that the scarcity of marine and fresh water organisms in the central stretch is due mainly to unsuitable tidal or salinity conditions.

Tidal sand and mud banks at the mouths of the Tees and the Tay contain roughly the same number of organisms per unit area. The height above low water of the intertidal areas of mud in the central part of the Tees Estuary varies considerably owing to the presence of wharves and retaining walls. Since the abundance of burrowing animals depends largely on the level of the available habitat in the tidal stretch, it is difficult to determine the true causes of local fluctuations in their numbers. Their density does not appear to be related to the concentrations of tarry products in the mud, except in the immediate neighbourhood of certain industrial outfalls. There appear to be suitable habitats for intertidal algae throughout the greater part of the Tees Estuary, but the distribution of the most common species varies considerably; this may be due in some way to the effects of pollution. On the whole, the fauna of the polluted Tees Estuary is similar both in variety and in abundance to that of unpolluted estuaries, except that in the Tees there are few, if any, fish living permanently in the central reaches and the numbers of certain shrimps are much smaller.

The plankton, or free floating organisms of the estuary, consists of fresh water species, mainly diatoms, washed down from the upper river and marine organisms carried into the Estuary mainly in the sub-surface current. In addition, a brackish water variety of a small marine crustacean is found. During the summer this copepod occurs in abundance and is distributed over the greater part of the Estuary; in the winter it is not nearly so abundant and its range is restricted to a short stretch in the central portion.

Various industrial effluents, many of them containing substances highly toxic to fish, are discharged into the Estuary. The most important of these are coke oven effluents, consisting of spent still liquors and effluents from coke oven gas coolers. The main toxic constituent of spent still liquors is the group of phenolic substances known as tar acids, and in effluents from gas coolers the most toxic constituent is cyanide. Approximately 4,400 lb. of tar acids and 1,800 lb. of cyanide are discharged daily. No other toxic substance enters the Estuary in large quantities. Cyanide is very much more toxic than tar acids, concentrations of the order of 0.01 to 0.02 part per 100,000, calculated as (CN), being sufficient to kill fish in less than an hour. Laboratory experiments showed that the toxicity of a solution of cyanide increases with rise of temperature and as the concentration of dissolved oxygen is reduced, but is little affected by additions of sub-lethal concentrations of tar acids.

In the spring of 1931 an extensive survey was carried out during the period when salmon and sea trout smolts were migrating through the Tees Estuary to the sea. As in the two previous years, large numbers of fish were killed in the polluted region. With the low prevailing water temperature, the concentration of dissolved oxygen remained at a moderately high level and was more than 50 per cent. of the saturation value until the end of the migration period, when it fell to between 40 and 50 per cent. In a laboratory experiment rainbow trout lived comfortably for 35 days in a stream of running water, the oxygen concentration of which varied between 37 and 58 per cent. with a mean value of 48 per cent. of the saturation value. Over short periods of a few days the



minimum oxygen requirements of trout were found to be considerably lower than these concentrations. During the migration tar acids were present in the estuary in concentrations of 0.01 to 0.03, and more rarely in amounts exceeding 0.05 part per 100,000; these are considerably lower than the minimum concentration required to kill fish. On the other hand, cyanides were present on most days during the migration in concentrations as high as, and sometimes exceeding, 0.02 part (CN) per 100,000, which is sufficient to kill fish in a short period. Samples of estuary water taken from the mortality stretch and found to be toxic to trout were rendered innocuous by the removal of cyanide. Moreover the colour of the gills of smolts found dying in the Estuary was brighter than that of normal fish, a characteristic symptom of poisoning by cyanide. All the evidence collected points to the fact that cyanide, discharged as a constituent of effluents from coke oven gas coolers, was the main cause of the mortality in 1931. It is also possible that in exceptionally warm spring weather the dissolved oxygen content of the water might fall so low as to be insufficient to support fish life.

Smolts were systematically netted, marked and released during the migration in 1931. Some of these marked fish were later recovered and were found to have remained in the estuary for periods up to 9 days. No relationship was found between the numbers netted on any day and the volume of water coming down from the upper river. The dead smolts collected provided information on the size, age, sex and food of the migrating fish. The collection was composed mainly of 2-year-old fish, and migration appeared to be dependent on their reaching a size above a certain minimum. Fish which did not grow to this length in two years migrated in the following season.

In view of the mortality of fish brought about in the Tees Estuary by cyanide, some experiments were carried out to determine the effect of cyanide on invertebrate animals. Of four crustaceans, the ranges of which are particularly restricted in the Tees, two were apparently unaffected by the maximum concentration normally found in the estuary, while two, the common shrimp and the chameleon shrimp, were susceptible to this concentration. It seems probable that the ranges of these latter animals are restricted by the presence of cyanides.

Both cyanides and tar acids undergo decomposition when diluted with water, and it is probable that a considerable loss of these substances occurs during the period in which they are carried to and fro in the Estuary. While the rate of decomposition of tar acids is markedly accelerated by the presence of sewage, that of cyanides is apparently unaffected. The breakdown of cyanides is, however, increased when they are diluted with estuarine water, and it is possible that this water contains a specific bacterial flora capable of bringing about their decomposition.

An examination was made of the methods by which the oxygen demand of the different types of polluting material entering the Estuary might be assessed and compared. In determining the rate at which dissolved oxygen is absorbed from solution by sterile industrial effluents it is essential that they should be diluted with water containing an appropriate bacterial flora; the diluent used was aerated estuary water of a constant salinity. The total oxygen demand of the sewage was estimated from the population served by the sewerage systems, the demand due to spent pickle liquors was calculated from the weight of ferrous iron discharged, and the oxygen demands of other industrial effluents were determined experimentally. It has been estimated that, of the total oxygen demand, nearly 60 per cent. is due to sewage, about 3 per cent. to spent pickle liquors and nearly 40 per cent. to other industrial effluents.

It was hoped during one period of smolt migration to remove cyanide from the coke oven effluents before discharge into the river in order to ascertain if the death of smolts could thereby be prevented. Several methods for the removal of cyanide were examined. A large scale experiment was carried out in which 5,000 gallons of effluent per hour were treated with lime and spent pickle liquor, a local waste product containing ferrous chloride; the cyanide was thus converted to ferrocyanide. The untreated effluent in 1 per cent. dilution killed fish in a few minutes, whereas the treated effluent in the same dilution was innocuous over a period of 24 hours. Unfortunately it was not possible to arrange for the treatment of all the effluents containing cyanide by this or other means during the 1932 migration.

As the result of the work relating to effluents from coke ovens, it has been concluded that the discharges of such effluents into the Tees could be greatly



reduced in quantity, and possibly eliminated, by modifications in the methods employed for cooling and washing the coke oven gas and by utilisation of waste liquids for quenching coke. Such modifications could readily be incorporated in designing new installations, but they would involve considerable alterations to existing plant. It is understood that installations of coke ovens to be erected in the future in the Tees area will be so designed as to avoid the discharge of any appreciable quantity of polluting effluent.

With regard to pollution of the estuary by sewage, this could be reduced, if considered necessary, by treatment of the sewage in efficient purification works or by discharging the sewage into the sea at a point some distance from the shore



## CHAPTER II

## GENERAL DESCRIPTION OF THE ESTUARY

The River Tees enters the North Sea through a long winding estuary flowing in a general north-easterly direction across a flat agricultural plain bounded by the Cleveland Hills to the south and the hills of Durham to the north. The limit of tidal effect is at High Worsall, some 25 miles from the sea, where there is a distinct rise of the river level at high water during springs. The upper Tees is a fast flowing stream, occupying, for the greater part of its length, a shallow and rocky channel, and above the tidal reaches it is nowhere navigable. The river is subject to considerable floods which often rise suddenly and subside as quickly. On one occasion, in October, 1932, the river rose so rapidly that three carts which had been used in removing gravel from the river bed had to be abandoned and were swept away. Owing to these sudden variations in the flow of the river, any estimate of the volume of water entering the estuary, unless based on continuous records, can be only a rough approximation to the true value. During the survey of the tidal reaches observations of the river height were made three times daily on a gauge erected on Croft Bridge near Darlington, and the relationship between the river height at this point and the volume of water passing was determined. The flow during the summer months is of the order of 10–20 million cu. ft. per 24 hours, and 40–50 million cu. ft. under normal winter conditions. The volume of water in the Estuary from Stockton to a point  $2\frac{3}{4}$  miles from the sea is, very roughly, 450 million cu. ft. at mean tide level, that is 25–45 times the daily supply of fresh water under summer conditions and approximately 10 times the supply under normal winter conditions. The relation between the volume of water in an estuary and that entering it from the river is of considerable importance in determining changes brought about by rainfall, temperature, and other factors.

When the water of the upper river enters the lower reaches at Yarm, it contains a considerable quantity of dissolved oxygen and is practically unpolluted in comparison with the water of the Estuary. It is, however, often highly coloured by peaty material washed out of pools on the moors. In reaction it is usually slightly alkaline except during spates, when it receives acid water from the peat bogs on the upland moors.

The River Skerne and all the tributaries from the Pennine Range join the main river before it becomes tidal, and below Yarm the only tributary of importance is the Leven, which enters it on the southern bank between Stockton and Yarm at a point about 17 miles from the mouth. The Leven rises in the Cleveland Hills and drains the low land south of the Tees. It was not possible during the survey to carry out any extensive observations of the variations in its flow, which normally in dry weather rarely greatly exceeds 5 per cent. of that of the Tees. The other tributaries entering below Yarm are even less important. Two small streams, Lustrum Beck and Billingham Beck, enter from the north but their flow is negligible compared with that of the main river. Greatham Creek, a small stream draining an area on the north of the Tees, enters by way of a channel through the Seal Sands. On the south bank the Old River, for a distance of about a mile before it enters the Tees, occupies what was formerly the bed of the main river, which, until the year 1810, formed at this point a large horseshoe bend. In 1810 the navigation of the river was greatly improved when its course was straightened by the cutting of a canal through the neck of this bend. In all, the tributaries entering the Estuary are relatively unimportant and, except in the case of the Leven, no attempt was made during the survey to gauge their flow.

The Estuary lying between Yarm Road Bridge and the sea, a distance of about 18 miles, flows through three markedly different types of country. From Yarm to Stockton, a distance of about seven miles, there are no important towns, and the country on both banks is mainly agricultural, a large proportion being under grass. The banks are steep and consist mainly of soil or grass-covered slopes, although in short sections they are faced with slag. The channel is very winding and is undredged, but is navigable by small vessels at high water. At



low water this stretch of the river is shallow and fast flowing and is entirely fresh throughout its length. The bottom is composed mainly of rocky shelves, covered in places with gravel or sand and, near Stockton, with deposits of clay.

After leaving this agricultural country the Estuary passes for a distance of about seven miles through a thickly populated district in which the main industries of Tees-side are concentrated. It is in this section that the bulk of the sewage and industrial effluents with which the Estuary is polluted are discharged. On the Yorkshire side the largest towns are Thornaby (21,200), Middlesbrough (138,500) and Eston (31,100); on the Durham side, Stockton (67,700) and Billingham (18,000); the populations given in brackets are based on the census of 1931. The domestic sewage of practically the whole of this area, from a total population of about 280,000, is taken by water carriage through sewers and discharged untreated into the Estuary between Stockton and Cargo Fleet. In all there are 49 main outfalls spaced throughout this section, the majority of them being rather below half-tide level and fitted with flap valves so that the sewage is discharged during a period of about two hours before and after low water.

Stockton, on the north bank, is an old-established port but the industrial area on the south bank, stretching in an almost unbroken line from Newport to Cargo Fleet, has been built up almost entirely during the past hundred years, following the discovery of iron ore in the Cleveland Hills. The main industry of the district is the production and working of iron and steel, and the greater part of these works are concentrated on the south bank of the Estuary. In all there are some 60 blast furnaces, many of which were closed down during the period of the survey. The glare in the sky at night when the furnaces are working is one of the characteristic features of the Tees-side district. For the purpose of smelting iron large quantities of metallurgical coke produced in by-product coke ovens are used. The gas manufactured at the same time is largely used in the plant itself, and the domestic supply of the town of Middlesbrough is taken from this source. By-products such as tar, naphthalene, ammonia and benzol are also recovered during the manufacture of the coke. The effluents which are produced during these processes are the most important type of industrial waste discharged into the Estuary. A large proportion of the iron produced is converted into steel in the district. There is, in addition, an important group of industries engaged in heavy steel constructional work, and shipbuilding and repairing is one of the main industries of the Estuary. Among the final forms of the manufactured steel are galvanized sheet and wire, and the cleaning of steel in hydrochloric acid before galvanizing produces the strong solution of ferrous chloride which constitutes another type of industrial effluent discharged into the Estuary. On the Durham bank, the main industries have been established during recent years and consist in the production of synthetic nitrogenous fertilisers and other chemical products. The minor industries of the district include the mining and preparation of salt, the manufacture of miscellaneous chemical products and of cement, basic slag, bricks, and glassware. In addition to the effluents produced in these various manufactures, very large quantities of Estuary water are pumped from the river and used for cooling purposes; the temperature of this water is thereby raised and in some cases the dissolved oxygen concentration is lowered.

The Estuary is an important seaport and is used by ships up to 13,000 tons gross tonnage. The number of vessels entering and leaving the port in 1931 was 2,961, with a net registered tonnage of over 3,000,000. The main imports are iron ore, iron and steel, and general merchandise, and the exports are iron and steel, chemicals, salt, coal and coke, slag and general goods.

In the central industrial section of the Estuary the banks are mainly slag or mud slopes and, in the lower reaches of this section, wharves, usually built with wooden piles, are almost continuous. The channel is dredged to a depth of not less than twelve feet at low water, and the bottom consists of soft black mud with patches of clay and occasionally of sand or gravel exposed by dredging. Below Cargo Fleet, the dredged channel runs for the greater part of its length between slag training walls built up to about half-tide level. Behind these on either bank are extensive mud or sand flats, which are covered to a depth of a few feet at high tide but which become dry on the ebb. Formerly the river divided and encircled the sand banks, which were the breeding place of large numbers of seals and were known as the Seal Sands. Land reclamation and the building of the training walls has resulted in the blocking of the northern channel about four miles from the sea. The channel remaining now drains the northern side of the Seal Sands and carries



away the waters of Greatham Creek. The lower part of this channel, known as Seaton Channel, which runs at right angles to the main channel and joins the latter just over a mile from the sea, is dredged and serves as an entrance to a shipyard and industrial works. The arm of the river which ran on the south side of the Seal Sands now forms the main dredged channel of the river. As the tide rises, water from Seaton Channel flows over the Seal Sands until at half-tide the training wall in the main channel is covered. On the ebb, as soon as this wall is exposed, water is prevented from flowing into the main stream, and during the remainder of the ebb drains off into the Seaton Channel. Part of the Seal Sands is now being reclaimed by the Tees Conservancy Commission.

On the south bank the sand and mud flats are flooded, like the Seal Sands, from a short blind channel near the Estuary mouth. The sand and mud banks become narrower towards the mouth and at the coast the river channel is guarded by the North and South Gare breakwaters, three-quarters of a mile apart. The depth at low water in the main stream is rarely less than 18 feet. The bottom consists mainly of sand, invaded at the upper end by mud from the central reaches.

The whole of the main channel below Stockton is essentially artificial in character, and since the year 1834 very large quantities of material have been removed from the bed by dredging. As an indication of the extent of the alteration which has been made in the depth of the river it may be mentioned that in 1863 the depth of water at the bar was  $3\frac{1}{2}$  feet: it is now 23 feet at low water. It appears, however, that the Estuary below Stockton has never, at least during the past century, been fordable<sup>(1)</sup>. At the mouth of the river the maximum range of springs is about 18 feet and the smallest range of neaps about  $4\frac{1}{2}$  feet.

The Tees formerly contained large and flourishing fisheries, and is stated to have produced "great abundance of excellent fish such as salmon, flounders, eels, smolts or sparling, etc."<sup>(1)</sup> Salmon and sea trout were netted by drag-net from the mouth as far inland as Dinsdale where there was a salmon-lock. At present the net fishery is confined to the neighbourhood of the Estuary mouth, where gently sloping sand banks allow sweep-nets to be worked. The weight of fish caught, both by netting at the Estuary mouth and by rod in the upper reaches, is now comparatively small. The great decline in the salmon and sea trout fishery is undoubtedly due to the serious pollution to which the Estuary is now subjected.

In order to understand the important bearing which the character of an Estuary, or even of a short length of it, has on the abundance of salmon and sea trout in the river as a whole, it is necessary to consider briefly the habits of these fish. Salmon and sea trout spend a great part of their life in the open sea. They ascend into the fresh water reaches of rivers to spawn, migrating usually during January to May, when they are known as "spring fish," or during the late summer and autumn when they are known as "summer" or "autumn fish." They may, however, enter fresh water at any time during the year. With the exception of the late-run fish, they are, when they leave the sea, in good condition and of a silvery appearance, and their tissues are well stored with fat. The eggs and sperm are deposited in gravel beds in shallow parts of the river or its tributaries, spawning usually taking place from September to January, principally in December. Whilst in fresh water salmon and sea trout do not feed regularly and after spawning the survivors descend to the sea in a very weakened condition; they are then known as "kelts." The young (alevins) when hatched are provided with yolk sacs which later disappear and the fry begin to feed. At the end of two years in the Tees salmon have usually attained a length of about 6 in. and sea trout 7 in. At the end of a period, which differs in different rivers but is usually two years in the Tees, the young fish assume a silvery appearance (the "smolt stage"), and migrate to the sea during the months of April, May and June. Two or more years are spent in the sea and the adult fish then return to fresh water to spawn. There is good evidence that most adult fish return to spawn in the river in which they were born. A polluted estuary forms a barrier to the ascent and descent of adult fish and to the seaward passage of the young smolts. As salmon and sea trout return mainly to their native river high mortality amongst the sea-going smolts must bring about a progressive decline in the stock of adult fish returning to the river.

As the result of pollution there are now few, if any, fish permanently living in the central part of the Tees Estuary, and there is widespread mortality amongst migratory fish. During the months of April, May and June, between Bassleton Wood and Middlesbrough, large numbers of smolts of both salmon and sea trout may be seen lying dead on the banks of the Estuary or floating helplessly on the

surface of the water. Adult fish also are occasionally seen dead on the banks, although in much smaller numbers. It is held by many observers that these do not generally attempt to ascend a river except during a spate from the upper reaches, and it may be that they thus make their passage of the Estuary under the most favourable conditions, since the water from the upper river is always less polluted and more highly oxygenated than that of the central reaches of the Estuary. It is certain that many adult fish are captured whilst in a dying condition and so escape record.

A general decline in the numbers of fish taken by rod in the upper reaches has occurred during the last 23 years, for which period records are available (Fig. 1), and there has been a general though less regular fall in the numbers of salmon and

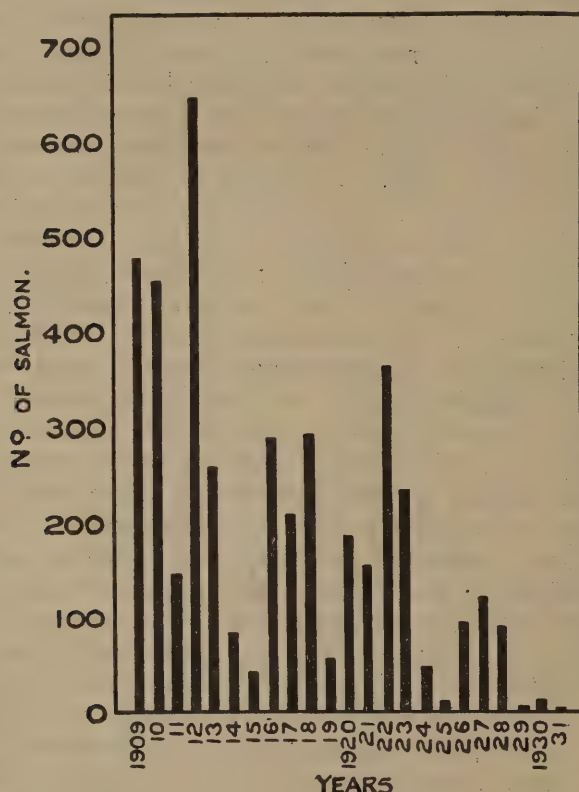


FIG. 1—Number of Salmon Caught by Rod in the River Tees

sea trout taken in nets at the Estuary mouth. It seems probable, however, that the returns from netting are a less reliable index of the effects of pollution in the Estuary than are records of rod catches, since some at least of the fish caught near the coast are not ascending the river but are passing the Estuary mouth on their way to other districts.

The causes of the mortality amongst fish migrating through the Estuary formed one of the problems studied during the survey.

#### REFERENCE

<sup>(1)</sup> BREWSTER, J. The Parochial History and Antiquities of Stockton-upon-Tees. John Richardson, London, 1829.



## CHAPTER III

## HYDROGRAPHICAL CONDITIONS

Near the mouth of a river there is always a stretch of brackish water where fresh water from the upper river mixes with salt water from the open sea. The length and position of this stretch depend on the size and speed of the river, the size of the estuary, and the movement of the sea water under tidal action. In a very large or swift river, this stretch will probably extend only a short distance up the estuary and may even be outside it in the open sea. In slow moving streams the mixture of salt and fresh water may extend a considerable distance inland. The length of the brackish stretch in a river varies also with the state of the tide. The Estuary of the Tees is long and for some time before it reaches the sea the river flows through flat country. At high water during springs, salt is perceptible at a distance of over 16 miles from the mouth, and from this point seawards the proportion of salt water increases until at the coast at high water the influence of fresh water is inappreciable, except during large floods from the upper river. The proportion of salt and fresh water at any given position in the central part of the Estuary is constantly changing with the movement of the water, the proportion of salt water increasing as the tide rises and decreasing as it ebbs. The tidal movement of the water also varies from day to day as the tidal range changes. Superimposed on these regular oscillations, there is the variable effect of floods or spates from the upper river, which tend to increase the proportion of fresh water in the Estuary as a whole. An exact knowledge of the distribution of salt water in the Estuary and the extent of its variability is of importance in a study of the Estuary as a whole since it can be used in estimating the movements of substances discharged into the Estuary, and it is one of the main factors which influence the distribution of animals and plants.

The proportion of salt and fresh water in a sample of estuarine water can be quickly determined. From a determination of the chloride content of a sample of Estuary water, the equivalent weight of total salts can be computed by means of Knudsen's Hydrographical Tables and the proportion of fresh and salt water calculated. The percentage of sea water in samples of a given salinity (that is a given concentration of total salts expressed as gm. per 1,000 gm.) is shown in Table 1. The salinity of sea water in Tees Bay has been taken as 34 gm. per 1,000 gm.

TABLE 1—*Relation between Salinity and Percentage of Sea Water in Estuarine Water*

Salinity Gm. per 1,000 gm.	Percentage of sea water (approx.)
34	100
30	88
25	74
20	59
15	44
10	29
5	15

## DISTRIBUTION OF SALINITY UNDER AVERAGE CONDITIONS

During the survey, a large number of salinity determinations were made throughout the Estuary at all depths and at all states of the tide. Most of these observations were made on samples which were also used for the determination of some other factor, and the salinity was used as a means of fixing approximately the position of the sample in the moving body of estuarine water. In addition, a number of observations were made at the time of high or low water at fixed positions in the Estuary, and it is mainly on these data that this account of the distribution of salt and fresh water is based.

The average salinity at 6 positions at high and low water and at different depths is shown graphically in Fig. 2. From the information contained in Fig. 2 isohalines have been drawn (Fig. 3) showing the vertical distribution of salinity

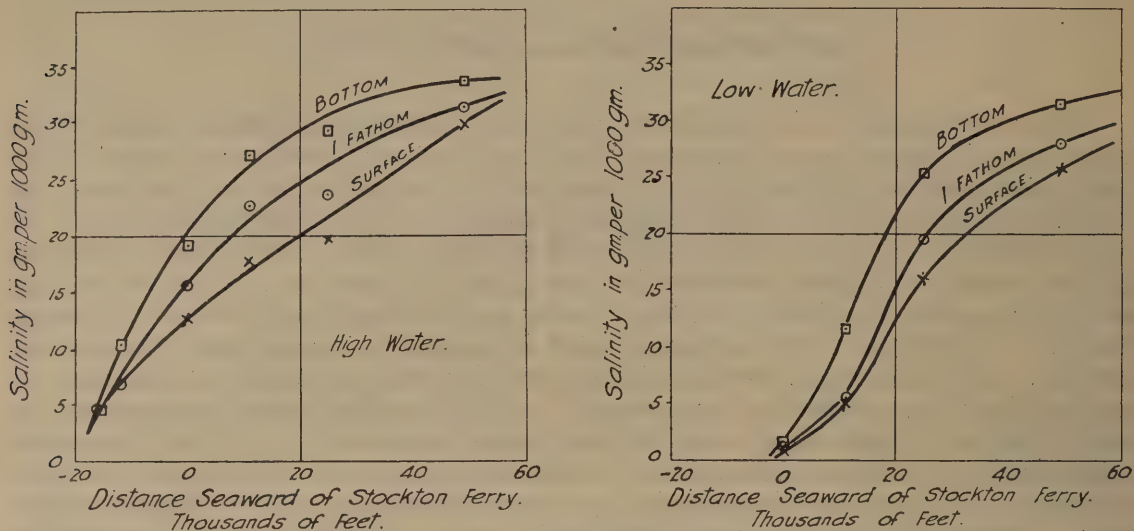


FIG. 2—Average Salinity at High and Low Water in the Tees Estuary

in a longitudinal section of the centre line of the Estuary. The most striking feature of the distribution of salinity in the central part of the Estuary is the marked difference between the surface and bottom layers. The vertical scale in Fig. 3 is greatly enlarged in comparison with the horizontal scale, so that the direction of the isohalines is actually more nearly horizontal than appears from the diagram.

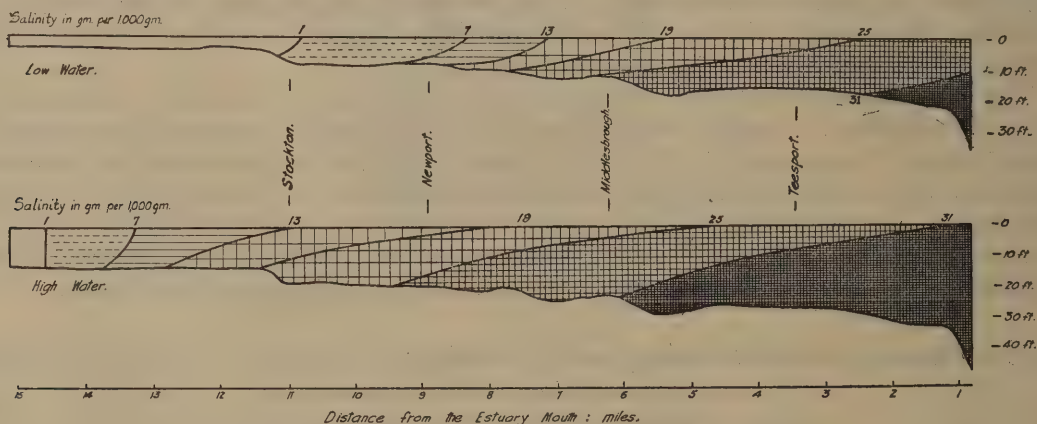


FIG. 3—Average Distribution of Salinity in the Tees Estuary

For example, the dip of the isohaline for salinity 25 is only about 5 feet per mile (1 : 1070) at both high and low water. Over short sections in the central part of the Estuary stratification is almost horizontal.

This distribution of salinity results from the circulatory current system of the Estuary, a description of which, based on a series of current measurements by meters at fixed positions, has already been published<sup>(1)</sup>. There are marked differences in the current speeds at different depths. On the ebb, the main force of the current is at the surface, while on the flood the upstream current is slower near the surface than in the deeper water. Whereas the net movement of the surface waters over a complete period of ebb and flood is seawards, the movement of the deeper layers is upstream. A similar circulatory system (Fig. 4), with fresh

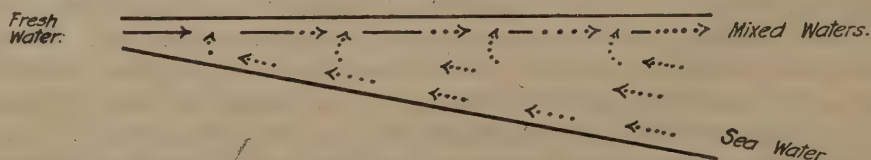


FIG. 4—Diagram illustrating the Circulatory System set up by Fresh Water running over Sea Water



water running out to sea over salt water, has been observed in other estuaries. Mixing between the layers is constantly taking place; fresh water picks up salt water and carries it out to sea and sea water moves upstream to replace that which is carried away. In the reaches above Stockton the mixing of the bottom and surface waters is relatively great, owing probably to the shallow, uneven and winding nature of the undredged river bed. In these reaches large upwellings of water can often be seen in calm weather, giving the surface a turbulent appearance similar to that seen in places in the lower Estuary where large volumes of water are discharged from pipes below the surface. As a result of this mixing the salinities of the surface and subsurface layers above Stockton are approximately the same during the ebb. The extent of the vertical mixing at Stockton is indicated in Fig. 5, in which is shown the salinity, at different depths, of the water passing upstream under Stockton Bridge during the flood and returning during the ebb;

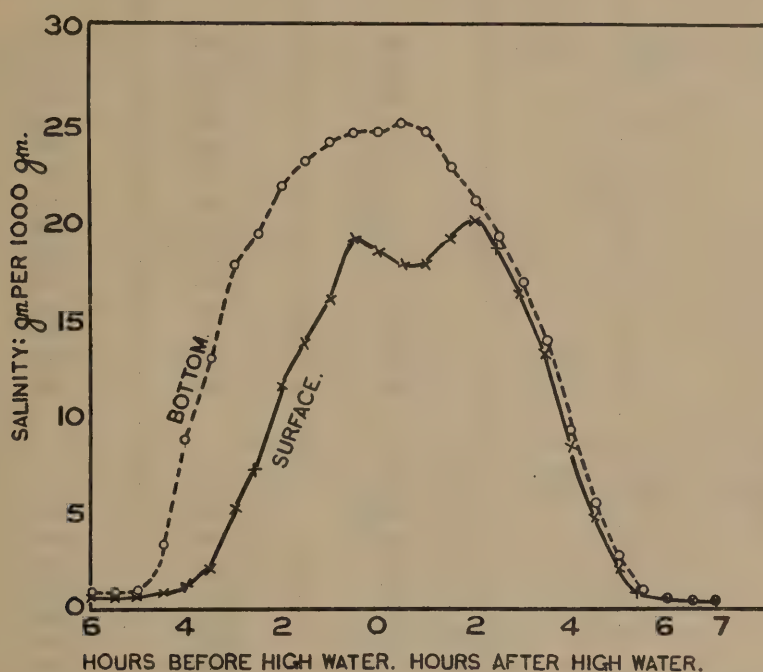


FIG. 5—Salinity of the Water passing Stockton Bridge on 6th June 1930 during a Flood and Ebb

there may also be some lateral mixing. The difference between the salinity of the surface and bottom layers, which on the flood amounts to about 10.5 gm. per 1,000 gm., disappears almost completely on the ebb. As the water which has been above Stockton at high water moves downstream into the deeper part of the Estuary, stratification is set up, as the movement on the surface becomes more rapid and continues for a longer time than the movement of the lower layers.

An attempt was made to follow the changes in salinity which occur at different depths as the water moves up and down the Estuary during the flood and ebb. Floats were used to follow the movement of the different layers of water. Usually a float consisted of a strong thin ash pole, with four large canvas vanes arranged as a cross at the lower end, weighted at the bottom and buoyed at the top so that it floated vertically. It was found, by comparing the rate of travel of a submerged float of this type with the speed of the current as determined by current meter, that the speed of the float was not appreciably different from that of the water at the level of the canvas vanes. For determining the speed of the surface current, Winchester bottles submerged as far as the neck were used. During the course of an ebb or a flood, samples were taken at intervals at the position occupied by the float, one sample at the depth of the canvas vanes or at the surface in the case of a surface float, and others at different vertical distances from this level. The changes in the salinity at different depths indicate the extent to which water at the level of the float vanes was being mixed with more saline or less saline water from below or above. Thirteen experiments in all were carried out, samples

being taken at the positions occupied by surface and  $1\frac{1}{2}$  or 2 fathom floats during flood and ebb. The results of four typical experiments are given in Table 2 and

TABLE 2—*Changes in Salinity in Water at Different Depths at Positions Occupied by Submerged Floats During the Flood and Ebb*

Depth of float and direction of movement.	Date.	Position. Thousands of feet seaward of Stockton Ferry.	Salinity of samples. Gm. per 1,000 gm.		
			Surface.	$1\frac{1}{2}$ Fathom.	Bottom.
$1\frac{1}{2}$ Fathom float, moving upstream.	4.8.32	20	3.0	12.2	15.7
		18	2.1	5.4	12.6
		$16\frac{1}{2}$	3.8	5.8	10.9
		13	1.3	5.8	6.3
		$9\frac{1}{2}$	1.3	2.6	4.7
		$5\frac{1}{2}$	1.3	1.5	2.3
		2	1.0	1.0	1.2
		— 1	1.0	1.0	1.0
		— $5\frac{1}{2}$	0.8	0.8	0.8
		— 10	0.6	0.6	0.6
		— 15	0.4	0.4	0.4
		— 19	0.4	0.4	0.4
		— 20	0.2	0.2	0.2
		— 22	0.2	0.2	0.2
Surface float, moving upstream.	4.8.32	21	4.3	15.8	20.7
		$20\frac{1}{2}$	6.9	19.1	22.7
		$19\frac{1}{2}$	13.7	18.2	22.7
		17	9.8	19.8	21.5
		15	12.2	20.4	22.7
		11	14.8	16.0	20.2
		8	15.7	19.1	20.2
		5	15.3	18.8	19.6
		1	15.7	16.9	19.1
		— $\frac{1}{2}$	12.0	16.9	18.6
		— 1	15.5	18.6	19.5
$1\frac{1}{2}$ Fathom float, moving downstream.	20.9.32	— 12	11.8	12.2	13.1
		— $11\frac{1}{2}$	11.3	12.6	14.2
		— 8	11.7	14.8	15.1
		— 6	12.6	15.3	16.4
		— $11\frac{1}{2}$	14.0	15.7	18.4
		2	14.9	16.2	19.5
		$5\frac{1}{2}$	15.7	16.7	20.9
		11	16.2	17.3	19.8
		$14\frac{1}{2}$	17.5	20.9	23.6
		18	18.4	20.6	23.6
		20	18.8	22.4	24.9
Surface float, moving downstream.	20.9.32	— 12	11.8	12.2	3.11
		— $11\frac{1}{2}$	11.8	12.4	15.3
		— 7	12.2	12.6	18.4
		— 3	14.8	16.2	17.9
		1	15.3	16.6	21.3
		5	16.0	17.9	24.1
		9	16.6	20.9	24.0
		$14\frac{1}{2}$	18.2	19.5	24.5
		$16\frac{1}{2}$	19.3	22.2	24.0
		22	20.9	22.2	28.1
		24	21.5	23.2	29.2
		26	21.6	25.6	30.8



the general nature of the salinity changes which occur are shown diagrammatically in Fig. 6.

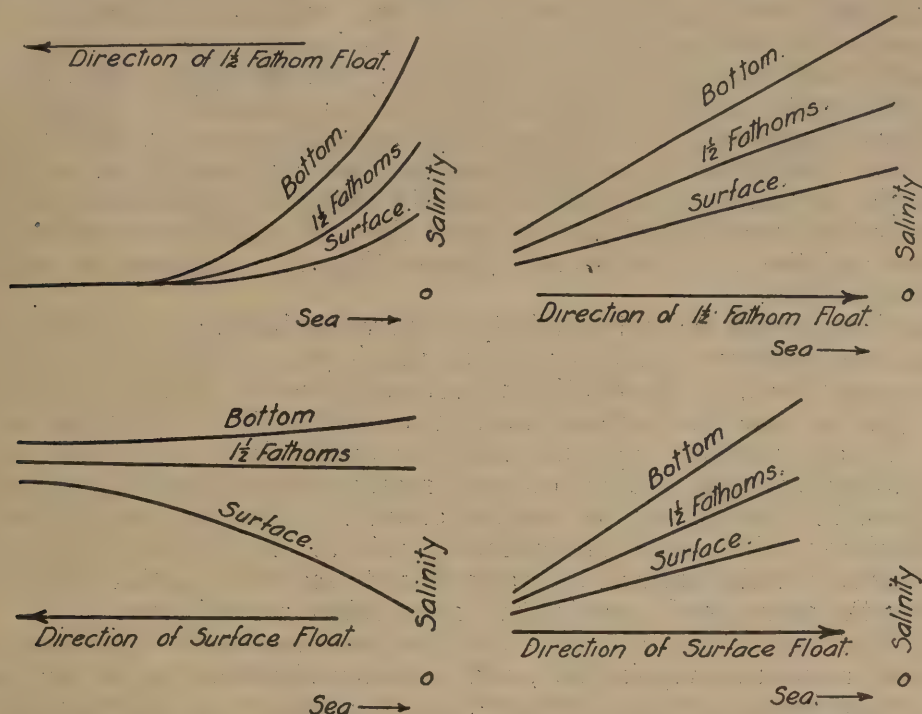


FIG. 6—Diagram illustrating the Changes in Salinity of Water at the Positions occupied by Floats during Flood and Ebb

During the flood, water at a depth of  $1\frac{1}{2}$  fathoms moves more quickly than the surface layer. The  $1\frac{1}{2}$  fathom float therefore moves upwards under a surface layer of decreasing salinity. The water at the level of the  $1\frac{1}{2}$  fathom float mixes with both this fresher water above it and with the more saline water below. The salinity of the bottom water below the float decreases as the float moves upstream, on account both of this mixing and because the velocity of the upstream movement at the bottom is not so great as at  $1\frac{1}{2}$  fathoms<sup>(1)</sup>. Finally, at a position above Stockton, water at all depths becomes completely mixed and the salinity gradient disappears. An interesting feature, in experiments in which a  $1\frac{1}{2}$  fathom float is followed for some distance above Stockton, is that after vertical mixing is complete the salinity, which is then usually 0.5 to 0.8 gm. per 1,000 gm., continues to fall although, within the range of upward movement of the float, it was not observed to drop completely to zero. Evidently mixing with fresh water is still taking place, although there is no apparent difference in the movement of layers at different depths at these positions above Stockton.

At low water the surface layer is less saline than the waters beneath it and during the flood these deeper waters travel upstream more rapidly than the surface layer. The water at a depth of  $1\frac{1}{2}$  fathoms beneath the position occupied by a surface float moving upstream therefore tends to become more saline, owing to its more rapid upstream movement, but there is also a decrease in salinity by admixture with the fresher water in the surface layer. In the experiment carried out on 4th August, 1932 (Table 2), the salinity at  $1\frac{1}{2}$  fathoms remained nearly constant. The main difference during the flood between the salinity changes at the positions occupied by a  $1\frac{1}{2}$  fathom and a surface float is due to the fact that the  $1\frac{1}{2}$  fathom float moves further upstream and reaches a position where vertical mixing is more complete. In both cases the vertical salinity gradient becomes less marked as the float moves upstream.

The vertical gradient is re-established during the ebb, when the water moves seawards into the navigable part of the Estuary where the greater depth, the absence of acute bends and the relative smoothness of the bottom allow the rapidly moving surface waters to ride over the lower layers without extensive mixing. At low water the Estuary waters are again stratified in layers inclined at a small angle to the horizontal, with the dense layers of the highest salinity beneath the lighter, less saline layers. During an ebb, the surface water over a  $1\frac{1}{2}$  fathom float moves faster downstream than the float, which is itself moving faster than the water below it<sup>(1)</sup>. The salinity of the water in the bottom layer increases towards the seaward end of the Estuary; as the  $1\frac{1}{2}$  fathom float travels at a greater speed over the top of this layer, the water beneath it becomes progressively more



saline, and the salinity of the water at its own level increases somewhat as a result of mixing. The surface water above the float would, if no mixing took place, become gradually less saline as a result of its greater speed, but the actual salinity change is a compromise between this fall and the increase due to passing over and mixing with lower layers of increasing salinity. On 28th July, 1929, the salinity of the surface water during an ebb at the positions occupied by a float 2 fathoms deep fell by about 3.5 gm. per 1,000 gm., and on 20th September, 1932, the salinity under similar conditions over a  $1\frac{1}{2}$  fathom float rose by about 8 gm. per 1,000 gm. The reduction in salinity at the surface over the deeper float (2 fathom) used in 1929 was greater than over the  $1\frac{1}{2}$  fathom float, since the relative movement between the surface and the 2 fathom layer is greater than that between the surface and the  $1\frac{1}{2}$  fathom layer.

There is a gradual rise in the salinity of the water below a surface float which is travelling down stream. In this case the rise is greater than that in the water below a deeper float, as the relative movement between the surface and bottom waters is greater than that between water at a depth of  $1\frac{1}{2}$  or 2 fathoms and at the bottom. In all cases the layering, which is partly destroyed during the flood when the water is moving into shallower and more turbulent reaches, is re-established during the ebb. In the shallow reaches above Stockton the deep saline waters and the surface fresher waters are intimately mixed. In the deeper reaches of the Estuary during the ebb the surface waters flow to sea with relatively little mixing, riding over the more slowly moving and more saline water below.

A distribution similar to that in the Tees was observed in the estuary of the Tyne during a short survey in 1931, and a similar stratification of the waters of Randers Fjord has also been reported<sup>(2)</sup>. In the estuary of the Tay, which was visited in 1930 and 1932, the salinity distribution was very different. In dry weather on a line near the southern shore there was only a very small vertical salinity gradient (the maximum observed difference between the salinity at the surface and bottom was 1 gm. per 1,000 gm.), and at times of fresh water floods the extent to which the fresh water remained unmixed at the surface was very much less than in the Tees. The estuary of the Tyne, like that of the Tees, has a deep, dredged channel and a relatively smooth bottom. The Tay is undredged and shallow and contains numerous sand banks, so that vertical mixing of the surface and sub-surface waters occurs to a much larger extent than in the artificially deepened estuaries of the Tees and Tyne.

An interesting phenomenon, which has been observed in many parts of the world, sometimes occurs in the Tees Estuary, when the dark coloured water of the central reaches is divided by a sharply defined line from the clearer water seaward of it. It is popularly supposed that this line is the boundary between pure fresh water on the one hand and pure sea water on the other. There is, in fact, a distinct and sudden salinity change at the junction of the two stretches, although the difference in salinity is relatively small. Thus, on 10th October, 1932, when the line was very clearly marked, the salinities of surface samples, taken some 5 yards apart above and below the boundary, were 24.9 and 32.4 gm. per 1,000 gm. respectively.

#### EFFECT OF FRESH WATER FLOODS ON DISTRIBUTION OF SALINITY

The account which has been given of the distribution of salt water is based on salinity values which are the averages of a series of determinations on samples taken at random during the whole period of the Tees investigation. Early in the survey it became apparent that the distribution of salinity in the Estuary was profoundly affected by variations in the flow of fresh water from the upper reaches. A record was, therefore, kept of the level of the upper river at Croft, above the limits of tidal action and below all tributaries of the Tees except the Leven. The level of water at this position was taken usually three times daily. In considering the effect of variations in the volume of fresh water entering the Estuary on the distribution of salinity, some difficulty arose from the fact that the time taken by water to flow from Croft to the Estuary, and through it to the sea, was not known. It was observed during the hydrographical survey<sup>(1)</sup> that a spate travelled from Croft to Yarm, at the head of the Estuary, in approximately  $5\frac{1}{4}$  hours. It has been estimated (Table 6) that fresh water may remain in the Estuary, after passing Stockton, from 3 to 7 days, the period being shorter for large than for small volumes of fresh water. The maximum effect of a spate on the distribution of salinity would, however, occur some time before the whole volume of water had reached the sea. In comparing distributions of salinity in the Estuary under



different conditions of upper river level, the average gauge reading on the day preceding the salinity determinations was taken as an index of the fresh water flow. This method can give only a rough approximation of the variations in the influx of fresh water to the Estuary. A short spate, following a period of dry weather and occurring on the day before a series of salinity determinations in the Estuary, will produce a smaller diluting effect than a long period of flood conditions. In addition, owing to the rapidity with which the upper Tees rises and falls, it is possible for a spate to occur, especially during the night, between two gauge readings. The average of the daily readings of the river height can be regarded, therefore, only as a general indication of the volume of fresh water entering the Estuary.

The salinity observations taken at high and low water in the Estuary have been divided into two groups. In the first group the average river level at Croft on the day preceding the observations did not exceed 1 ft. on the gauge, and in the second the corresponding river level was between 1 ft. and 2ft. 6 in. Observations made on days following larger fresh water floods than this have not been included. The first group represents the salinity distribution under average summer conditions, and the second, the distribution under normal winter conditions. The mean salinities at high and low water for different positions in the Estuary are given in Table 3. From these data, graphs similar to Fig. 2 have been drawn, and these have been used in the construction of the isohalines in Figs. 7 and 8.

TABLE 3—*Mean Salinities at High and Low Water in the Estuary*

Number of determinations in brackets

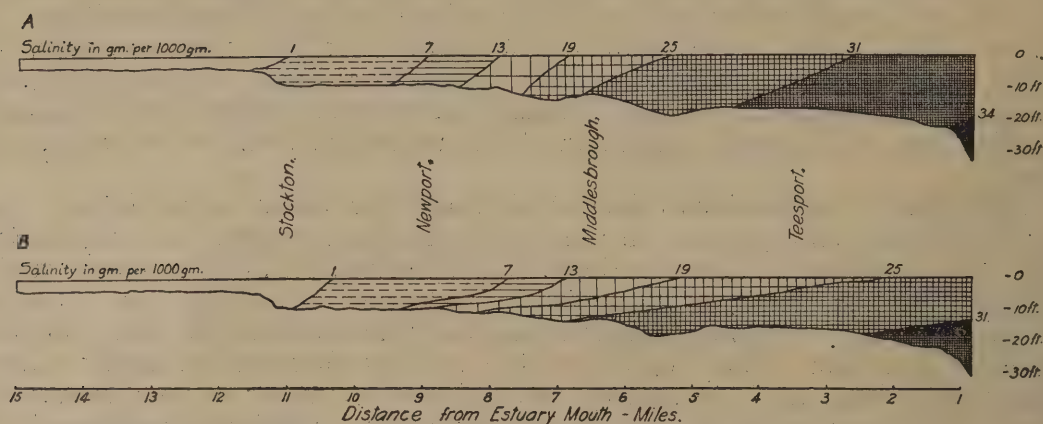
Height of river at Croft not exceeding 12 in. on day before salinity determinations.

Position Thousands of feet seaward of Stockton Ferry.	High Water.			Low Water.		
	Surface.	1 Fathom.	Bottom.	Surface.	1 Fathom.	Bottom.
—16	11·5 (9)	11·8 (7)	11·3 (8)	0	0	0
—12	15·3 (7)	16·0 (6)	15·6 (6)	0	0	0
0	16·5 (8)	19·8 (8)	23·1 (5)	1·0 (11)	1·9 (6)	2·5 (6)
11	22·4 (10)	25·8 (10)	27·5 (7)	7·1 (12)	7·7 (12)	10·1 (8)
25	27·3 (9)	29·8 (10)	32·2 (7)	22·4 (12)	24·9 (35)	26·5 (9)
49	33·6 (5)	34·0 (5)	33·9 (5)	29·0 (2)	32·4 (2)	33·3 (2)

Height of river at Croft 12 in. to 2 ft. 6 in. on day before salinity determinations.

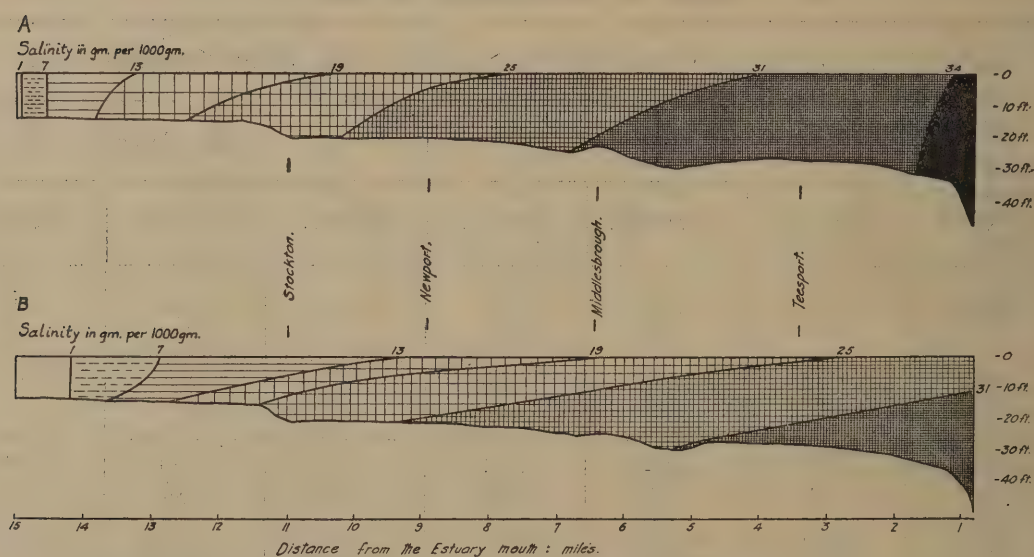
—16	2·4 (9)	—	2·8 (6)	0	0	0
—12	7·3 (7)	4·6 (4)	9·9 (4)	0	0	0
0	9·4 (2)	12·2 (3)	21·0 (2)	0·4 (4)	0·7 (3)	0·6 (2)
11	13·8 (5)	21·9 (5)	27·4 (5)	2·8 (5)	3·3 (5)	12·9 (4)
25	18·9 (12)	22·8 (12)	28·9 (11)	15·7 (10)	19·3 (40)	26·2 (9)
49	26·3 (3)	28·4 (3)	33·5 (3)	25·9 (7)	27·9 (6)	31·5 (5)

The effect of floods from the upper river on the distribution of salinity in the Estuary is very marked, causing a large dilution in the surface waters for a long distance down the Estuary. An inspection of Figs. 7 and 8 shows that for fresh



A.—Normal Summer Conditions. Height of river at Croft not exceeding 1 ft.  
B.—Normal Winter Conditions. Height of river at Croft over 1 ft. but not exceeding 2 ft. 6 ins.

FIG. 7—Distribution of Salinity in the Tees Estuary at Low Water



A.—Normal Summer Conditions. Height of river at Croft not exceeding 1 ft.  
B.—Normal Winter Conditions. Height of river at Croft over 1 ft., but not exceeding 2 ft. 6 ins.

FIG. 8—Distribution of Salinity in the Tees Estuary at High Water

water floods in which the river height does not rise above 2 ft. 6 in. at Croft, the salinity of the bottom waters in the central part of the Estuary is very little lower at low water than under dry weather conditions, though at high water the difference is appreciable. Fluctuations in salinity comparable with those brought about at the surface by moderate fresh water floods are only caused in the bottom waters by exceptionally heavy spates. This relative immunity of the deeper waters from large changes in salinity is an important factor in considering the distribution of aquatic animals and plants in the Estuary, since the majority of living organisms are incapable of withstanding wide fluctuations in the salt content of the water.

At the seaward end of the Estuary, during dry weather, the diluting effect of fresh water is not very marked. Stratification in ordinary dry weather is thus confined mainly to the central part of the Estuary. The influence of the very high fresh water floods is considerable even at the mouth at high water. Thus, during a



spate on 6th September, 1931, when the upper Tees was well above normal winter level, and the Skerne was also exceptionally swollen, the salinity at the Estuary mouth at high water was only 7 gm. per 1,000 gm. at the surface and 25 gm. at the bottom. The greatest difference in salinity between the surface and bottom waters on this day was 20 gm. per 1,000 gm. at Middlesbrough at high water. During fresh water floods of this magnitude, the water in Tees Bay, over a large area near the mouth of the Estuary, is often strongly coloured by yellowish suspended material brought down from the upper reaches.

The maximum and minimum salinity values which were observed in the Estuary during the survey are shown in Fig. 9; the variation was marked, especially in the surface waters.

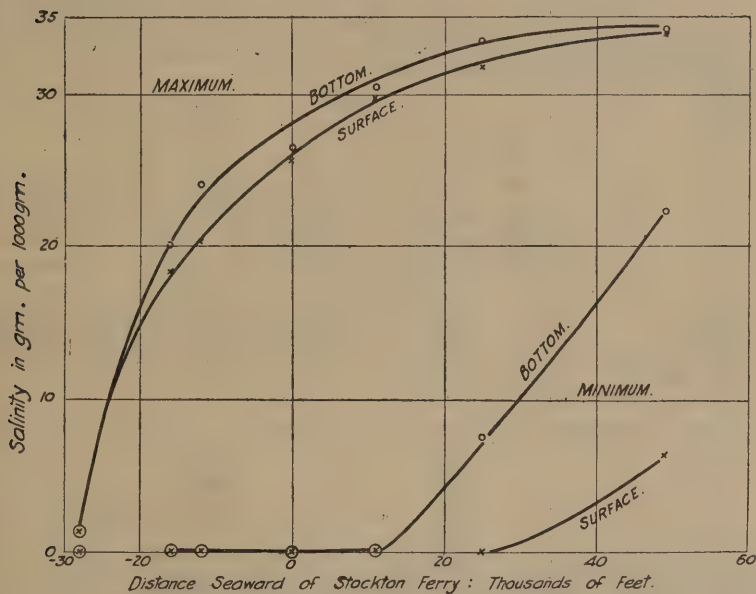


FIG. 9—Maximum and Minimum observed Salinities in the Tees Estuary

#### EFFECT OF RANGE OF TIDE ON DISTRIBUTION OF SALINITY

In addition to the disturbances caused by fresh water floods in the distribution of salinity in the Estuary, variations occur which are due to the periodic fluctuations in the level of water at the Estuary mouth. At springs a given mass of water will be pushed further upstream at high water, and will return to a position further seawards at low water than during neaps. Owing to the large disturbances caused by floods from the upper reaches, a considerable amount of work would be necessary to define exactly the effect of varying range of tide on the distribution of salinity in the Estuary. The data which it was possible to obtain during the survey are only sufficient to show the general trend of the salinity movements which accompany changes in the tidal range. It is probable that the details of the distribution of salinity are not representative of truly average conditions, especially at the upper end of the Estuary where the effect of varying river flow is most intense.

In order to eliminate as far as possible the effect of changes in fresh water flow from the upper river, the salinity observations made under dry summer conditions, when the height of the upper river at Croft did not exceed 9 in., have been extracted from the basic data and divided into two groups, showing observations taken during springs and neaps (Table 4).

TABLE 4—*Relation Between Range of Tide and Salinity at High and Low Water in the Estuary*

Height of River at Croft on day before salinity observations, 6 in. to 9 in.  
Number of observations in brackets  
Salinity in gm. per 1000 gm.

Position  Thousands of feet seaward of Stockton Ferry.	Range of Tide not exceeding 12 ft.						Range of Tide exceeding 12 ft.					
	High Water.			Low Water.			High Water.			Low Water.		
	Surface.	1 Fathom.	Bottom.	Surface.	1 Fathom.	Bottom.	Surface.	1 Fathom.	Bottom.	Surface.	1 Fathom.	Bottom.
—16	12.1 (2)	—	6.9 (1)	0	0	* 0	11.5 (4)	11.9 (4)	12.1 (4)	0	0	0
—12	14.5 (2)	—	10.7 (1)	0	0	0	16.1 (3)	16.6 (3)	17.0 (3)	0	0	0
0	14.6 (6)	18.8 (6)	22.8 (3)	1.0 (5)	1.5 (1)	0.8 (3)	22.4 (2)	22.8 (2)	23.7 (2)	0.2 (4)	1.4 (3)	0.8 (1)
11	19.4 (6)	24.2 (6)	26.1 (4)	10.7 (3)	11.7 (3)	14.2 (2)	28.3 (2)	28.7 (2)	30.4 (1)	6.5 (8)	7.1 (8)	10.4 (4)
25	25.8 (6)	28.8 (6)	32.1 (3)	23.7 (3)	27.4 (8)	27.9 (3)	30.5 (1)	30.6 (1)	31.6 (1)	20.4 (4)	24.2 (8)	23.3 (2)
49	33.6 (3)	34.0 (3)	34.2 (2)	31.6 (1)	31.7 (1)	32.8 (1)	33.9 (1)	34.3 (1)	34.0 (1)	32.0 (1)	33.1 (1)	33.7 (1)



From Table 4 graphs similar to Fig. 2 were drawn, and from these Figs. 10 and 11, showing the distribution of salinity at high and low water for tides with ranges of more than 12 ft. and less than 12 ft., were constructed. There is a noticeable difference in the shape of the isohalines at springs and neaps. During

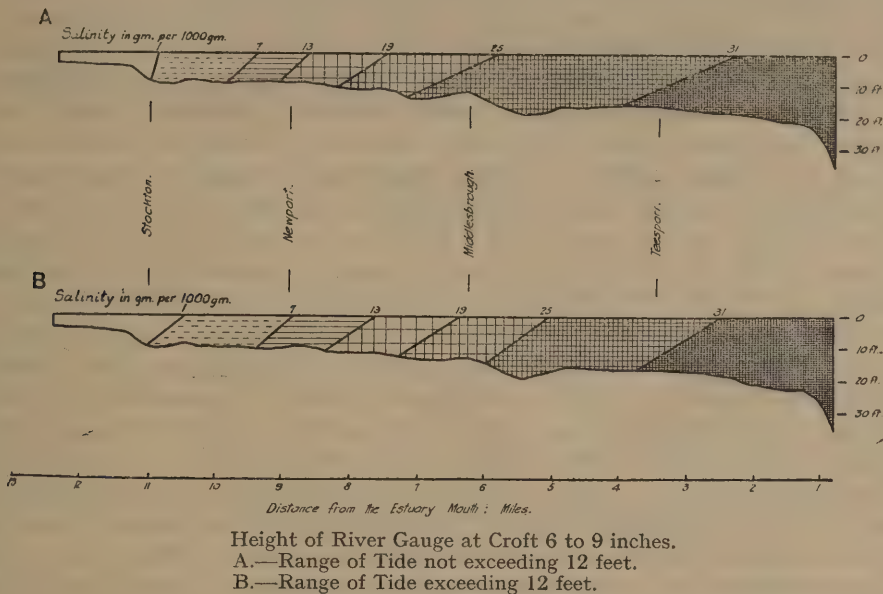


FIG. 10—Effect of Tidal Range on the Distribution of Salinity in the Tees Estuary at Low Water

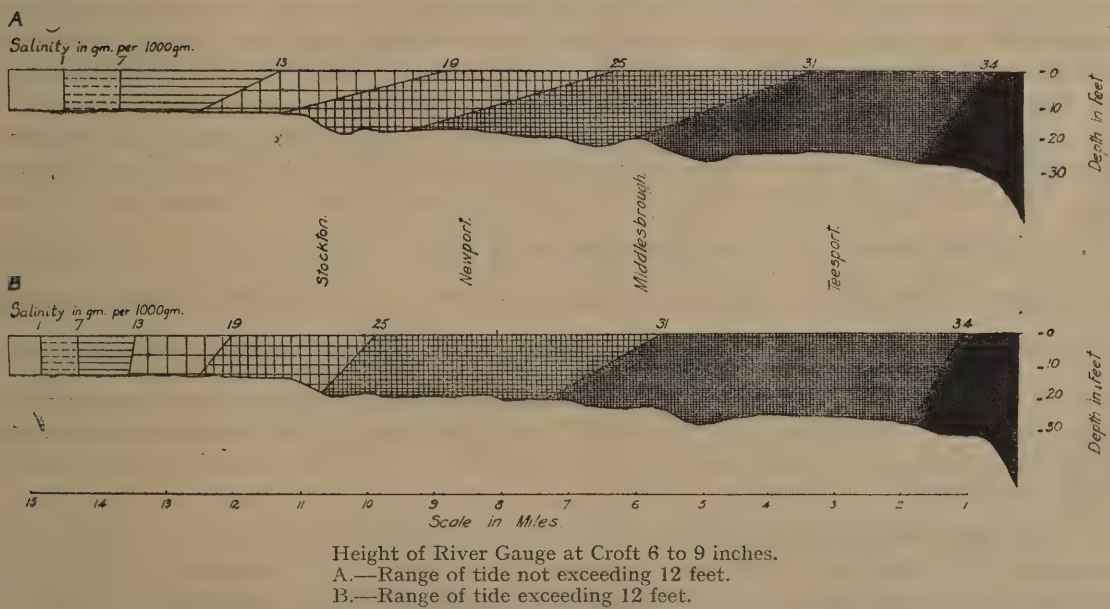


FIG. 11—Effect of Tidal Range on the Distribution of Salinity in the Tees Estuary at High Water

springs, saline water penetrates further upstream at high water and recedes at low water to a position nearer the Estuary mouth than during neaps. The difference in the salinity distribution brought about by changes in the tidal range is of a different type from that caused by floods from the upper river. The tidal movement brings about an alteration in the movement of the water in the central part of the Estuary as a whole, whereas an increased inflow of fresh water affects mainly the salinity of the surface waters.

## TIME TAKEN BY FRESH WATER AND EFFLUENTS TO PASS THROUGH THE ESTUARY

One of the objects of investigating the salinity conditions in the Estuary was to estimate the time between the discharge of an effluent into the Estuary at any given position and its final discharge into the waters of the open sea. In the case of a fresh water stream into which an effluent is discharged, if the volume of the effluent and the rate of flow of the stream are known, the concentration of the effluent at a point sufficiently far from the outfall to allow of complete mixing may be calculated. The estimation of the effect of a series of effluents on the waters of the Tees Estuary is a much more difficult problem. Here, the stream is represented by a long stretch of water moving to and fro under tidal action and changing in volume with the tidal height and range. Fresh water is continuously entering the upper end of this reservoir, while at the lower end brackish water passes out to sea on every ebb and clean sea water flows in on the flood. It is this new water, both fresh and salt, which is available for the dilution of effluents discharged into the Estuary. If the substances discharged were soluble and chemically stable, their concentration in the general body of the Estuary waters would attain and remain at the value resulting from their dilution with the incoming water from the upper river and the sea. If, however, the substances discharged are decomposed after their dilution with the waters of the Estuary, their concentration will be lower than that given by this simple relationship, the difference depending on their rate of decomposition and the length of time they spend in the Estuary. Before comparing the estimated and observed concentrations of constituents of unstable effluents in the Estuary, it is necessary, therefore, to estimate the time taken by their passage to the sea and the extent of their decomposition during this period.

An estimate of the time spent in the Estuary by a given body of fresh water coming in from the upper reaches has been made by comparing the average total volume of fresh water in the Estuary with the volume entering from the upper river. Under the hypothetical condition of uniform flow from the upper river and constant range of the tide the distribution of salinity would attain a condition of equilibrium—being the same every high water, every half ebb, every low water and every half flood. The volume ( $V_1$ ) of fresh water entering the Estuary from the upper river during every tidal period of 12 hours would then equal the volume which passes out to sea during the same period. If the distribution of salinity at some particular state of the tide and the capacity of the Estuary are known, the volume ( $V_2$ ) of fresh water within the Estuary can be calculated. Then  $\frac{V_2}{V_1}$  equals the mean time, expressed in tidal periods, spent within the Estuary by a mass of fresh water before passing out to sea. Some of the fresh water will naturally pass out to sea in a shorter time than  $\frac{V_2}{V_1}$  tidal periods, and some will remain longer within the Estuary. This hypothetical condition does not actually occur, as both the inflow of fresh water and the range of the tide are constantly changing. The time thus calculated can therefore be no more than a very rough approximation.

The total volume of water in the Estuary was estimated from a series of soundings supplied by the Tees Conservancy Commission. The areas of 63 cross-sections were calculated, the sections being close together where the contour of the bottom varied appreciably and more widely spaced in reaches with an even bottom. The volume was calculated for a water level at the River Tees entrance (5th Buoy Lighthouse), 9 ft. above the datum of the Admiralty Tide Tables (1929–32); this is approximately the mean sea level over a long period of springs and neaps. The volumes of water refer only to the central channel between the training walls; no allowance was made for the water which flows over the Seal Sands and over the flats on the south shore near the mouth of the Estuary. These calculations of water movement in the Estuary are, therefore, comparable with those made during the hydrographical survey<sup>(1)</sup>. It was pointed out in the report on that survey that the Seal Sands assist the fresh water to reach the sea, since they dry out at each low water. In the work recorded in the present report the time taken by fresh water to travel from Stockton to 9th Buoy front light, a distance of 14,000 ft. from the Estuary mouth, was calculated. Normally the water



between 9th Buoy front light and the sea is practically salt, and although the time taken by water to reach 9th Buoy front light will be rather less than that taken to reach the Estuary mouth, this small difference should be compensated for by the accelerating effect of the Seal Sands.

The volume of fresh water was estimated from salinity determinations over a long period of neaps and springs (Table 3) and the cross-sectional areas, assuming a mean height of 9 ft. above Admiralty datum. The mean salinities at half tide and for all depths under normal summer and winter conditions for four positions between Stockton and the sea are given in Table 5. The salinity at a given position at half tide was taken as the arithmetic mean of the values at high and

TABLE 5—*Average Salinity at a Tidal Height of 9 Feet above Admiralty Datum in the Estuary*

Position  Thousands of feet seaward of Stockton	Salinity in gm. per 1,000 gm.	
	Summer conditions	Winter conditions
0	10·8	7·4
11	16·8	13·7
25	27·2	22·0
49	32·7	28·9

low water. The mean value so obtained is not strictly correct, especially at positions near the ends of the Estuary, where the water is either completely fresh or completely salt during a large part of the tidal cycle. The errors in the two cases, however, tend to neutralise one another. In calculating the percentage of fresh water from the salinity values of Table 5, the salinity of the water of Tees Bay, which is assumed to be pure salt water, was taken as 34·0 gm. per 1000 gm.

The volume of fresh water entering the Estuary from the upper reaches was calculated from observations, taken three times each day, of the height of the river at Croft. Although these readings are a fair guide to the volume of fresh water entering the Estuary they do not accurately represent the mean conditions over 24 hours, for no readings were taken during the night, and it was found that large fresh water floods might occur between one reading of the gauge and the next.

In the dry weather series of salinity determinations in the Estuary, the mean of 684 gauge readings at Croft was 8–9 inches, corresponding to a fresh water flow past Middleton-one-Row of about 10 million cu. ft. per 24 hours. In the second series, taken under conditions of greater fresh water flow, the mean of 552 readings at Croft was 1 ft. 8 ins., corresponding to a flow of about 44 million cu. ft. per 24 hours. These volumes refer to water passing Middleton-one-Row, but below this point several small tributary streams enter the river, by far the largest being the Leven, which joins the Estuary between Yarm and Stockton. At times the flow of the Leven may be unusually great while that of the Tees is normal. A series of observations made with a current meter in the Leven on 30th April, 1932, when it was at about normal winter level, showed that the volume of water entering the Estuary was approximately 2·3 million cu. ft. per 24 hours, equivalent to about 5 per cent. of the flow of the Tees on the same day. In the determination of fresh water flow made during the hydrographic survey, the total volume of water from the Leven and other small streams entering the Tees below Middleton-one-Row and sewage discharged into the Estuary was taken as 10 per cent. of the flow of the Tees at Middleton-one-Row<sup>(1)</sup>. On the same basis the total mean volume of fresh water entering the Estuary whilst the salinity observations were being made was about 11 million cu. ft. per 24 hours for the dry weather series and about 48 million cu. ft. for the wet weather series.

Using the data given in Table 5 for the salinity of the Estuary water under different conditions of fresh water flow, the volumes of adjacent compartments

of the Estuary calculated from soundings, and the volume of fresh water entering the Estuary during the salinity observations, the times taken by fresh water to pass from Stockton to a number of positions seaward have been calculated and are given in Table 6.

TABLE 6—*Estimated Mean Time Taken by Water Entering the Estuary at Stockton to Reach Positions Further Seaward*

Distance travelled seaward of Stockton	Total volume of water between Stockton and position reached	Volume of fresh water in water between Stockton and position reached		Time taken by water to travel from Stockton to given position.	
		Millions of cu. ft.		Days	
		Upper river not exceeding 1 ft. in depth at Croft.	Upper river 1 ft. to 2 ft. 6 ins. in depth at Croft.	Upper river less than 1 ft. in depth. Average flow 11 million cu. ft. per 24 hours.	Upper river 1 ft. to 2 ft. 6 ins. in depth. Average flow 48 million cu. ft. per 24 hours.
Feet	Millions of cu. ft.				
4,200	13	8.7	9.8	0.8	0.2
8,100	27	16.8	18.9	1.5	0.4
13,600	48	27.5	31.2	2.5	0.7
19,200	82	41.0	47.8	3.7	1.0
24,700	128	53.5	66.0	4.9	1.4
28,900	170	60.8	79.2	5.5	1.6
32,100	222	66.8	92.1	6.1	1.9
36,900	307	73.4	109.2	6.7	2.3
40,800	380	77.0	120.3	7.0	2.5
43,800	446	79.8	128.7	7.3	2.7

The time taken by fresh water to reach the sea, determined from observations of salinity and fresh water flow, is the mean time taken by fresh water distributed throughout the whole depth of the Estuary. Substances which remain in the surface layer will be discharged into the sea in a shorter time, since there is a strong net downstream movement of this layer. On the other hand, material which is sufficiently heavy to sink into the bottom layers may be carried upstream by the bottom current. It appears that the mean time is considerably less during conditions of high fresh water flow. This is in general agreement with the conclusions reached as the result of the hydrographic survey<sup>(1)</sup>. As the result of current measurements it was concluded that, with the upper river at Croft at a mean depth of about 1 ft., the time taken by water to pass to the sea from a position 2,000 feet seawards of Stockton was about  $2\frac{3}{4}$  days. This applied to water moving only in a layer from the surface to a depth of 2 fathoms. If the whole depth of the Estuary were included the time would be greater, owing to the net upstream movement of the bottom water. The calculation did not take into account backwaters where the velocity of the tidal current is exceptionally low. If allowance is made for these factors there is a fair agreement between the rate of movement of fresh water to the sea as estimated by the two methods.

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<sup>(2)</sup> JOHANSEN, A. C. Randers Fjords Naturhistorie. C. A. Reitzel, Copenhagen, 1918. Chapter 3.



## CHAPTER IV

## EFFECT OF SEWAGE AND INDUSTRIAL EFFLUENTS ON THE DISTRIBUTION OF DISSOLVED OXYGEN

The central part of the Tees Estuary is subject to pollution by untreated domestic sewage from a population of about 280,000 people living in towns on the Estuary banks. In addition it receives large quantities of industrial effluents arising mainly from processes connected with the production and working of iron and steel. A detailed account of these effluents is given in Chapters XII and XIII, where the toxicity of their various constituents is discussed. The most important industrial wastes discharged are produced during the recovery of by-products from coke oven gas and of these there are two distinct types :

- (1) Spent still liquors from plants using the semi-direct method of ammonia recovery.
- (2) Effluents consisting of Estuary water which has been used for cooling coke oven gas by direct contact in plants operating the direct process and, in one case, the semi-direct process of ammonia recovery.

The qualitative composition of the two kinds of effluent is in some respects different although certain constituents are common to both.

It has long been known that sewage is decomposed and oxidised by bacterial action when diluted with water containing dissolved oxygen. Raw water-borne sewage contains a high proportion of nitrogenous organic matter and large numbers of bacteria capable of effecting its decomposition. After its discharge into the Estuary, part of this organic material is decomposed into simpler substances. Early in the decomposition process ammonia is produced and, if oxygen is available, may be later oxidised to nitrite and, finally, to nitrate.

Industrial effluents containing organic matter are, in general, also capable of oxidation by bacterial action. One method of disposing of the spent still liquor produced during the separation of ammonia from coal gas by the indirect process of recovery, consists in treating it on biological filters or with domestic sewage at a sewage disposal works ; this method is not in operation on the banks of the Tees. The spent still liquor produced on Tees-side from coke oven plants employing the semi-direct process of ammonia recovery is similar in composition to the effluents from the indirect process, and one of the main constituents of both is the group of phenolic substances known as tar acids. A more detailed description of the different types of effluent and an account of the progress of their oxidation when diluted with water containing oxygen in solution is given in Chapter XVI. Under the conditions existing in the Estuary, where dissolved oxygen and a supply of bacteria are normally present, they are all capable of oxidation at a fairly rapid rate.

The necessary oxygen is derived from two main sources ; part of it is in solution in the fresh water coming down from the upper reaches or in sea water entering from the mouth, and part is directly absorbed from the air through the surface of the Estuary water itself. The water entering the Estuary from the upper river and the sea is always approximately saturated with dissolved oxygen, so that the volume of oxygen supplied to the Estuary from these sources depends very largely on the volume of water coming in ; this is dependent on the rainfall in the case of fresh water and the tidal range in the case of sea water. Some information is available on the rate of oxygen absorption by de-aerated fresh and salt water under laboratory conditions. Adeney and his co-workers<sup>(1)</sup> ascribe the aeration of quiescent columns of water largely to the effect of evaporation of the water surface which by cooling the exposed layer causes it to sink, carrying with it dissolved oxygen. The factors affecting the rate of absorption of oxygen from the air by a mass of water of uniform depth and surface area are stated to be :

- (1) The degree of deoxygenation of the water. The velocity of absorption becomes greater as the difference between the partial pressure of oxygen in the water and the atmosphere is increased.
- (2) The humidity of the air. The rate of aeration is lowered as the humidity increases.
- (3) Salinity. The rate of oxygen absorption is greater in saline solutions than in fresh water. The optimum salinity is stated to be about 15 gm. per 1,000 gm.

- (4) Wind. Agitation of the surface of the water by wind increases the velocity of aeration.
- (5) Temperature. The weight of oxygen absorbed by a given volume of water in unit time does not differ materially at temperatures from  $0^{\circ}$  to  $30^{\circ}\text{C}.$ <sup>(2)</sup>. At the higher temperature, however, water is saturated with a smaller concentration of dissolved oxygen than at the lower. Hence the rate at which the percentage saturation of de-aerated water increases by absorption of oxygen from the air is greater the higher the temperature.

In the Tees Estuary, where there is a steep and constantly changing vertical salinity gradient, and where the waters are subjected to varying degrees of agitation by wind, tides and river traffic, the estimation of the volume of dissolved oxygen taken up from the air would be very difficult. The rate at which dissolved oxygen is removed by the bacterial oxidation of sewage and other organic matter is markedly increased by moderate increases of temperature. As the water temperature rises, therefore, the increased bacterial activity tends to lower the dissolved oxygen content while the increased rate of aeration which follows tends to raise it.

To obtain a reliable estimate of the changes in oxygen concentration from time to time it was necessary to carry out a series of surveys covering the whole of the Estuary, samples being taken at various depths at each sampling station. Considerable variations are produced when sudden floods occur in the upper reaches, since the dissolved oxygen content of the comparatively unpolluted fresh water is always higher than that of the Estuary water. The distribution and movements of the water in the central part of the Estuary vary continuously within wide limits under the influence of tidal movements and of varying fresh water flow. It is to be expected that these changes in the distribution of fresh and salt water will be accompanied by changes in the distribution of dissolved oxygen within the Estuary.

#### DISTRIBUTION OF DISSOLVED OXYGEN

The data on which this account is based were obtained in two ways. The majority of samples were taken from a launch running through the Estuary, the state of the tide usually being different from day to day. Determinations of the dissolved oxygen concentration, the temperature, the salinity and other constituents were carried out on these samples. In addition series of samples were taken under conditions as nearly comparable as possible in so variable a body of water as an estuary. These samples were drawn at the time of low water from a position opposite the laboratory at Cleveland Shipyard, Middlesbrough, and at a depth of one fathom. Altogether, 2,322 determinations of dissolved oxygen were made on samples taken from the Estuary during the course of the survey.

The relation between the dissolved oxygen concentration and the temperature in the series of samples taken at Cleveland Shipyard at low water is shown in Fig. 12. These samples were taken at irregular intervals, and the height of the

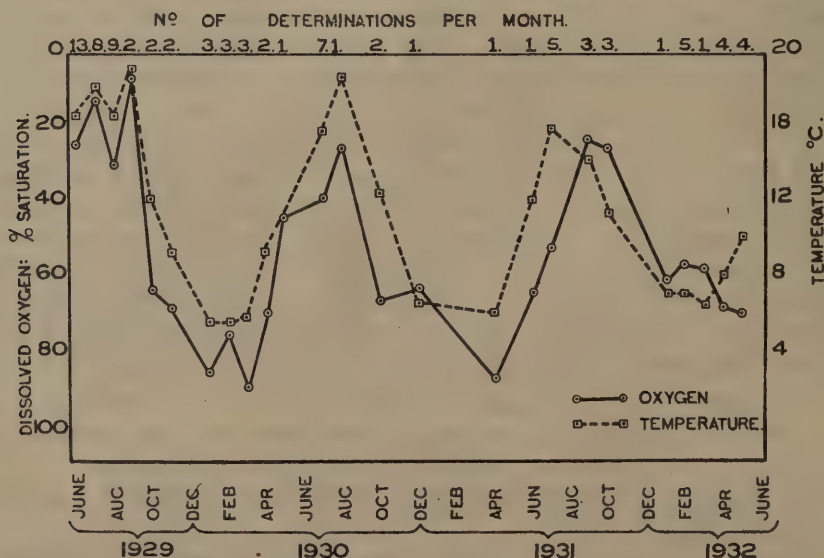


FIG. 12—Relation between Dissolved Oxygen Concentration and Temperature in Samples taken at Low Water at Cleveland Shipyard



upper river and the range of tide varied widely during the series. As a measure of the variation in conditions it may be mentioned that the salinity varied from approximately 2 to 30 gm. per 1,000 gm. These differences have been partly smoothed out by using for comparison the average values for dissolved oxygen and temperature for all the samples drawn during each month. There is an obvious correlation between the dissolved oxygen concentration and the temperature, high temperatures being accompanied by low concentrations of dissolved oxygen.

In considering the results of surveys in which samples were taken at a constant depth on each of a number of days from a launch working as rapidly as possible through the Estuary, it was noticed that the dissolved oxygen concentration was always relatively high at both ends of the Estuary, but fell steadily to a minimum value as the central stretch was approached. The minimum values occurred in water with a fairly small salinity range of approximately 15 to 20 gm. per 1,000 gm. There was also generally a vertical dissolved oxygen gradient similar to the vertical salinity gradient, and the minimum oxygen values occurred in water of salinity 15 to 20 gm. per 1,000 gm., whether the samples were taken from the surface or from the bottom at a position further upstream. The basic data were examined to determine whether this relation, at a given temperature, between the salinity and dissolved oxygen concentration of estuary water did exist irrespective of the depth from which the samples were taken (Table 7).

Table 7 does not contain the whole of the data but only those for temperature ranges within which large numbers of observations were available. The differences between the oxygen concentrations of comparable samples from different depths are irregular, the concentration being sometimes greatest at the bottom and

TABLE 7—*Dissolved Oxygen Concentration, Salinity, and Temperature of Samples of Water from Different Positions and Depths in the Estuary*

Average Dissolved Oxygen as Percentage of Saturation Value  
Number of determinations in brackets

Temp. °C.	Depth S=Surface. 1F=1 Fathom B=Bottom.	Salinity Range. Salinity in gm. per 1,000 gm.										
		0-1	1-5	5-9	9-12	12-15	15-18	18-21	21-24	24-27	27-30	30-33
7-8	S	86 (13)	87 (6)	83 (10)	—	80 (4)	77 (2)	76 (5)	72 (1)	71 (1)	—	—
	1F	87 (10)	83 (5)	83 (5)	73 (5)	78 (5)	77 (7)	75 (6)	73 (3)	73 (3)	86 (2)	95 (4)
	B	87 (5)	—	78 (2)	70 (1)	85 (4)	70 (5)	77 (3)	70 (6)	73 (4)	79 (8)	96 (1)
10-11	S	82 (12)	78 (15)	71 (21)	67 (15)	61 (9)	57 (12)	50 (3)	53 (5)	54 (5)	72 (4)	90 (3)
	1F	83 (11)	70 (8)	69 (12)	61 (9)	58 (14)	57 (9)	56 (7)	52 (8)	65 (6)	69 (5)	91 (6)
	B	86 (4)	68 (2)	64 (4)	58 (5)	55 (4)	54 (3)	61 (10)	66 (19)	70 (18)	78 (39)	92 (9)
12-13	S	84 (10)	74 (15)	69 (23)	59 (29)	57 (43)	57 (36)	67 (14)	60 (18)	71 (6)	71 (4)	—
	1F	84 (6)	79 (8)	76 (9)	64 (7)	72 (1)	67 (7)	62 (3)	71 (13)	74 (8)	85 (10)	80 (9)
	B	84 (6)	78 (3)	59 (5)	51 (4)	51 (5)	53 (7)	55 (6)	73 (3)	57 (4)	65 (6)	76 (3)
15-16	S	76 (5)	66 (8)	59 (9)	50 (14)	41 (15)	41 (22)	40 (35)	50 (20)	49 (26)	60 (10)	—

TABLE 7 (continued)—*Dissolved Oxygen Concentration, Salinity, and Temperature of Samples of Water from Different Positions and Depths in the Estuary*  
Average Dissolved Oxygen as Percentage of Saturation Value  
Number of determinations in brackets

Temp. °C.	Depth S=Surface 1 F=1 Fathom B=Bottom.	Salinity Range. Salinity in gm. per 1,000 gm.										
		0-1	1-5	5-9	9-12	12-15	15-18	18-21	21-24	24-27	27-30	30-33
15-16	1F	77 (7)	67 (6)	54 (11)	56 (7)	47 (13)	47 (13)	48 (15)	60 (28)	57 (45)	64 (56)	—
	B	81 (1)	60 (1)	50 (5)	42 (2)	31 (2)	34 (3)	38 (7)	46 (4)	38 (21)	45 (14)	—
17-18	S	76 (2)	65 (8)	53 (4)	34 (5)	35 (5)	27 (9)	31 (12)	41 (3)	55 (2)	67 (1)	—
	1F	80 (15)	64 (9)	43 (3)	33 (8)	31 (10)	29 (7)	30 (18)	32 (14)	34 (26)	23 (4)	—
	B	—	—	—	29 (1)	23 (1)	22 (1)	—	27 (1)	—	—	—

sometimes at the surface. On the whole the evidence suggests that the dissolved oxygen concentration of water of a given salinity at a constant temperature is practically independent of the depth from which the sample is drawn. It must be emphasised that the mean dissolved oxygen values given in Table 7 are the averages of series of widely-differing values. Large, irregular and rapid variations occur in the oxygenation of the Estuary, and an account of these and an explanation of their causes could only be given after a close study of the oxygenation of the Estuary waters from day to day and examination of a large number of observations.

Since the dissolved oxygen concentration of estuary water of a given salinity and temperature does not differ considerably for samples at different depths, the whole of the basic data may be divided into groups in each of which the salinity and temperature are approximately the same, so that the differences in the average dissolved oxygen concentrations of the groups may be compared. In Table 8 the data are grouped in this way. The temperature range in each

TABLE 8—*Dissolved Oxygen Concentration (as Percentage of Saturation Value) of Water of Different Salinities and Temperatures*  
Number of determinations in brackets

Temp. °C.	Salinity Range. Salinity in gm. per 1,000 gm.											
	0-1	1-5	5-9	9-12	12-15	15-18	18-21	21-24	24-27	27-30	30-33	>33
0-7	88 (87)	88 (39)	84 (21)	80 (18)	79 (16)	77 (17)	76 (13)	75 (18)	79 (12)	85 (22)	94 (8)	—
7-10	88 (57)	82 (41)	76 (42)	69 (23)	65 (25)	71 (34)	67 (32)	68 (24)	71 (27)	79 (43)	91 (21)	103 (1)
10-13	81 (43)	75 (51)	68 (66)	59 (78)	55 (74)	55 (72)	61 (37)	63 (65)	67 (45)	74 (63)	85 (23)	93 (9)
13-16	80 (42)	74 (38)	63 (49)	59 (46)	51 (54)	45 (50)	46 (74)	54 (69)	53 (116)	65 (115)	78 (38)	—
16-19	79 (20)	64 (21)	55 (18)	38 (19)	37 (25)	33 (31)	31 (42)	35 (39)	36 (49)	28 (9)	—	—
19-21	—	56 (8)	45 (7)	39 (6)	16 (20)	14 (10)	9 (10)	13 (19)	12 (8)	7 (3)	—	—



group is 3° C. in all cases except in the first group where the range is from 0 to 7° C., but in this group there are only a few observations at temperatures lower than 4° C. The salinity range in most groups is 3 gm. per 1,000 gm., but there are two groups in which the range is 4 gm. per 1,000 gm., and two have a range of only 1 gm. per 1,000 gm. The limits of temperature and salinity in each group were chosen in order that there might be, as nearly as possible, an equal number of observations in each group. From Table 8 the curves in Fig. 13, showing the relationship between temperature, salinity and dissolved oxygen concentration of the Estuary waters, have been constructed.

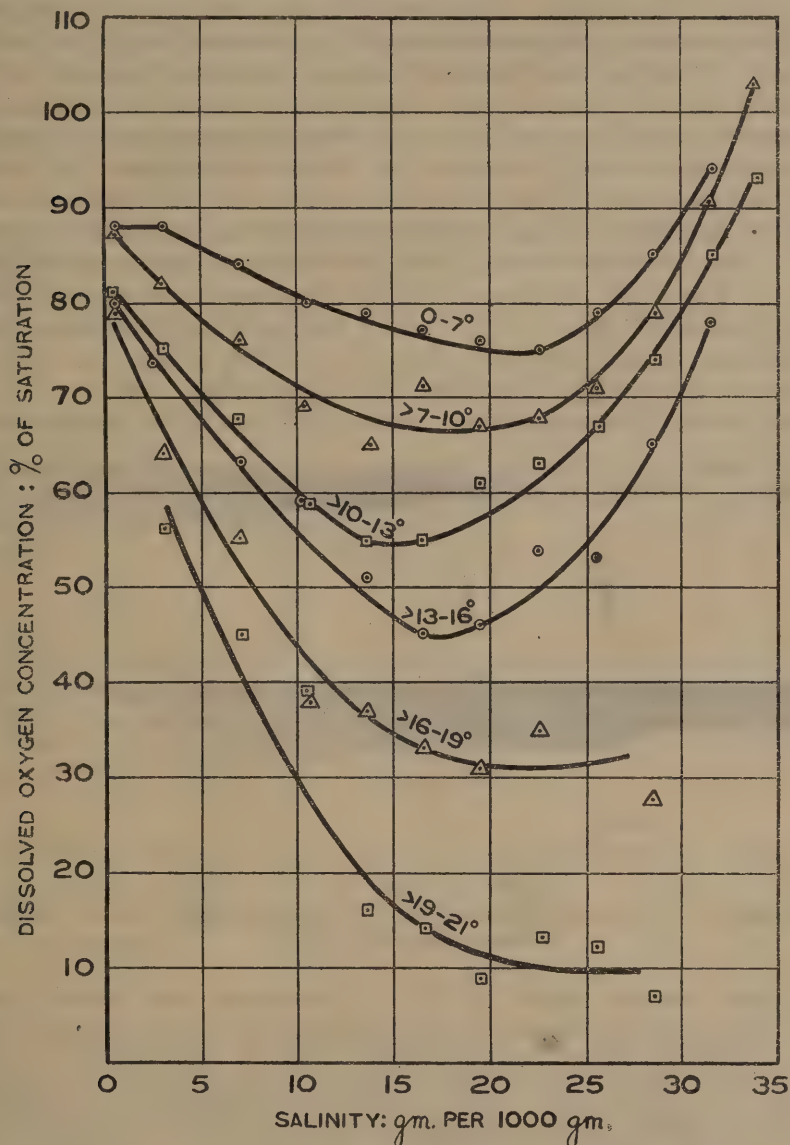


FIG. 13—Relation between Salinity, Temperature, and Dissolved Oxygen Concentration in the Tees Estuary

The level of oxygenation in water from the upper end of the Estuary with a salinity not greater than 1 gm. per 1,000 gm. did not fall appreciably below about 80 per cent. of the saturation value, even at the highest temperatures recorded. In calculating the average dissolved oxygen concentration of this group, the values for samples of zero salinity were included only when the samples were drawn from a position immediately above the limit of saline water. The oxygen concentration at this point was always lower than that in the fresh water reaches immediately above. At Yarm, at high water, the lowest dissolved oxygen concentration observed during the survey was 82 per cent. of the saturation value. The fresh water entering the Estuary was always highly oxygenated, and the effect of its addition to the polluted estuarine water was always beneficial. At the seaward end of the Estuary, for temperatures up to 16° C., the oxygen concentration of water of a salinity above 30 gm. per 1,000 gm. never fell appreciably below 80 per cent. of the saturation value; the sea thus constitutes another source from which highly oxygenated water enters the Estuary and raises the concentration of dissolved oxygen in the polluted water. At temperatures up

to 16° C., the greatest deoxygenation occurs in water with a salinity of 15 to 25 gm. per 1,000 gm., but at temperatures above 16° C. the salinity of the water in the stretch of maximum deoxygenation is higher. This would appear to be due to the fact that high temperatures occur usually in periods of dry weather, when, owing to the reduced flow of the upper river, the Estuary water is more saline.

In Chapter III it was shown that the salinity distribution in the Estuary could be represented by a series of isohalines, almost horizontal in the central reaches and approaching the vertical at both ends of the Estuary. Since the dissolved oxygen concentration at a given temperature is approximately constant in water of a given salinity whatever its depth, it follows that there is in the central part of the Estuary a vertical dissolved oxygen gradient similar to the vertical salinity gradient already described. From the normal distribution of salinity under dry summer conditions and from the relation between the dissolved oxygen concentration and the salinity shown in Fig. 13 the normal distribution of dissolved oxygen at high and low water, at a temperature of 13° to 16° C., has been calculated. This distribution is shown in Fig. 14 which represents longitudinal sections of the Estuary with lines drawn in to mark the boundaries of areas of different oxygen concentrations. The belt of most highly deoxygenated water lies between Newport and Middlesbrough at low water and above Stockton at high water. The observations at a fixed position at low water from which Fig. 12 was constructed were taken at the position marked "Middlesbrough" in Fig. 14. The most polluted stretch of the Estuary waters lies not far from this position at low water,

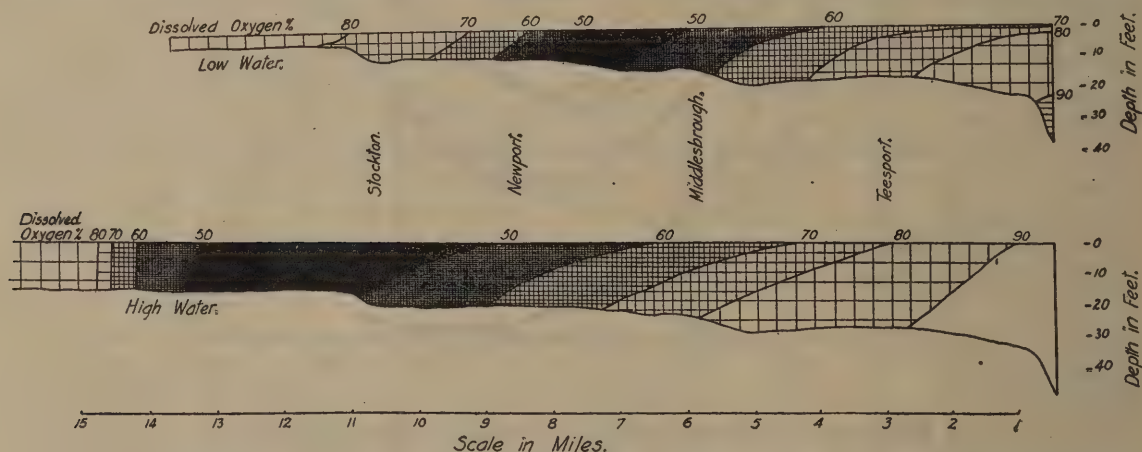


FIG. 14—Distribution of Dissolved Oxygen in the Tees Estuary under normal summer conditions. Temperature 13° to 16° C.

so that the oxygen values shown in Fig. 12 represent very nearly the minimum conditions of oxygenation found in the Estuary at any particular temperature. The extensive vertical mixing which takes place in the shallow reaches above Stockton during the flood tide is well shown and the diagrams indicate the circulatory current movements in the Estuary which have been mentioned in connection with observations of currents and salinity distribution. Unpolluted salt water makes its way up the Estuary from the sea, travelling along the bottom and mixing slowly with the more polluted water above it. Relatively unpolluted fresh water travels down from the upper reaches, and runs seawards mainly in the surface layers. In the section of the polluted reach above Stockton extensive mixing of the water occurs, and on the ebb part of the polluted water is discharged into the sea, mainly in the surface layers.

A comparison of Fig. 14 with the diagrams showing the distribution of salinity in the Estuary in dry and in wet weather (Figs. 7 and 8) indicates the effect on the distribution of dissolved oxygen of a flood from the upper reaches. A sudden influx of unpolluted fresh water increases the concentration of dissolved oxygen in the Estuary, washes part of the polluted Estuary water out to sea, and causes a general lowering of salinity, especially in the surface layers. Since a flood from the upper river thus affects both the oxygen concentration and the salinity of the Estuary water, the oxygen concentration of mixed water of a given salinity varies little with the volume of fresh water entering the Estuary.

The distribution of dissolved oxygen found on any particular day is usually of the same type as that shown in Fig. 14, which is representative of average conditions. This has been demonstrated on many occasions by the examination



of samples of water collected from a launch travelling as rapidly as possible from one end of the Estuary to the other.

The general conclusion is that the main factor affecting the degree of oxygen concentration is the water temperature. As the temperature rises, the activity of bacteria which bring about the oxidation of sewage and industrial effluents increases, and the rate at which oxygen dissolved in the Estuary waters is used in the oxidation processes becomes correspondingly greater. The absorption of oxygen from the air is insufficient to replace that absorbed by the accelerated oxidation processes and the concentration of oxygen in the Estuary water accordingly falls. There are also, however, other causes of rapid fluctuations in the concentration of oxygen. The increased oxygenation, especially of the surface waters, caused by spates from the upper river has already been mentioned. It is probable that further disturbances arise from variations in the rate at which oxidisable substances are discharged into the Estuary. For example, sewage is only discharged at about the period of low water. It is likely that heavy material in the sewers is flushed out after rain and the load of polluting matter discharged is then temporarily increased. The concentration of dissolved oxygen found on any day will probably depend not only on the temperature when the observations are made but, to some extent, on the temperature of the Estuary during the period immediately before sampling.

#### DISTRIBUTION OF THE PRODUCTS OF SEWAGE DECOMPOSITION

Usually samples taken at low water opposite Cleveland Shipyard for dissolved oxygen determinations were also used for determinations of "free and saline ammonia," albuminoid ammonia and nitrite. The maximum and minimum values observed during the period 1929 to 1931 are given in Table 9.

TABLE 9—*Maximum and Minimum Concentrations of Ammonia, Albuminoid Ammonia and Nitrite at Cleveland Shipyard at Low Water*

	Number of observations.	Nitrogen.	
		Parts per 100,000.	
		Maximum.	Minimum.
Free and Saline Ammonia	61	0.400	0.040
Albuminoid Ammonia	61	0.082	0.008
Nitrite	80	0.017	0

From a more detailed examination of the data there appears to be some connection between the concentrations of these nitrogenous substances and the temperature of the water. The average values for four ranges of temperature are given in Table 10. The product most affected is the free and saline ammonia,

TABLE 10—*Relation Between Temperature and Concentrations of Ammonia, Albuminoid Ammonia and Nitrite at Cleveland Shipyard at Low Water*

Temperature range. °C.	Nitrogen. Parts per 100,000 as		
	Free and Saline Ammonia.	Albuminoid Ammonia.	Nitrite.
4 to 8	0.14	0.028	0.005
8 to 12	0.17	0.025	0.005
12 to 16	0.18	0.029	0.006
16 to 20	0.24	0.028	0.007

the average concentration of which, over the temperature ranges considered, rose by about 70 per cent. The concentration of nitrite also increased but that of albuminoid ammonia remained about the same. These results refer only to samples taken at low water opposite Cleveland Shipyard. Some information is available on the concentration of nitrite in different parts of the Estuary. Several series of samples were taken from a launch running from one end of the Estuary to the other, and the grouped results of these observations are given in Table 11. These results show an increase in the concentration of nitrite as the water temperature rises. The general distribution is of the same type as that of dissolved oxygen deficiency, the maximum values of nitrite occurring in the highly deoxygenated water in the central stretch of the Estuary where the salinity is from 15 to 25 gm. per 1,000 gm. An example showing the distribution of nitrite at different depths throughout the Estuary is given in Fig. 15, where the results of a series of observations made 1 to 2 hours after high water are plotted on a longitudinal section of the Estuary.

TABLE 11—*Distribution of Nitrite in the Estuary*  
Concentrations of Nitrite as parts N per 100 million

Date.	Water Temperature at Cleveland Shipyard at High Water °C.	Salinity Range.					No. of deter- minations.
		Salinity in gm. per 1,000 gm.					
		0-7	7-14	14-21	21-28	28-35	
9.12.29	6½	1-2	1-3	1-3	1-2	1-0	36
7.3.30	7	0	0-1	0-3	1-0	0	24
30.10.29	10	1-4	3-5	4	5-3	3	35
24.10.29	11	3-4	4-5	6-7	6-3	4-1	27
9.8.29	15	2-4	4	4-3	3	—	14
13.8.29	15	—	5	5	5	4	18
3.9.29	16	2-6	6	6-7	7-5	—	23
6.9.29	16½	—	—	—	13-7	6-3	16
19.9.29	16½	2-6	8-13	20-26	26-16	11-6	19
11.9.29	17	—	8	8	8-5	7-3	24

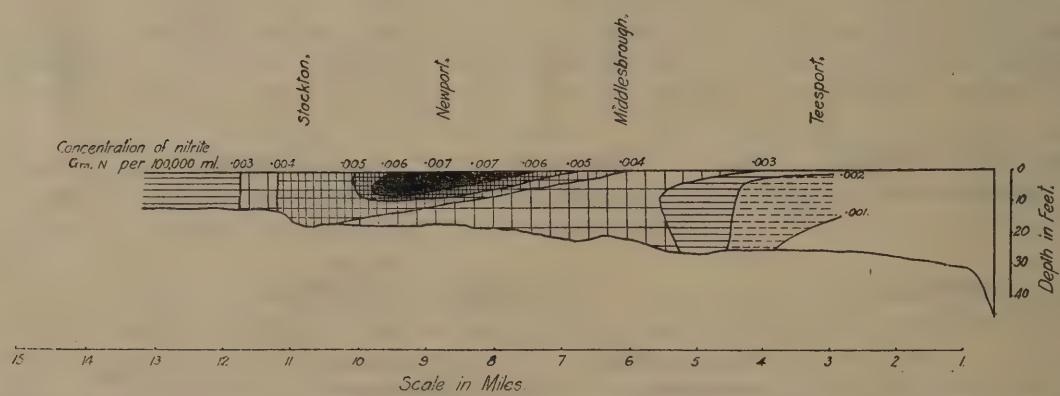


FIG. 15—*Distribution of Nitrite in the Tees Estuary on 24th October, 1929, 1 to 2 hours after High Water*

Again, the composition of the water above Stockton is the same at all depths, after the vertical mixing which has taken place during the flood tide. Below Stockton there are almost horizontal strata containing different concentrations of nitrite. At the mouth, there can be seen the wedge of pure sea water, containing only a low concentration of nitrite, which has made its way up the Estuary along



the bottom during the flood. On the day when the observations from which Fig. 15 is drawn were carried out, the maximum nitrite content was found in the surface waters. This does not always occur, and on some occasions the maximum observed concentrations were in water from the bottom. In general the distribution of nitrite appears to be much less regular than that of dissolved oxygen concentration. It is this patchy distribution that probably explains why the concentration of nitrogenous decomposition products in samples taken at Cleveland Shipyard at low water varies so much more widely than the concentration of dissolved oxygen.

## REFERENCES

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## CHAPTER V

CERTAIN CHEMICAL AND PHYSICAL CHARACTERISTICS OF THE  
ESTUARY WATERS

The water in the central reaches of the Tees Estuary is predominantly a mixture of varying proportions of sea and fresh water, but its composition is modified by the presence of sewage and industrial effluents. During the Tees survey no attempt was made to determine the composition of the water in detail, except where it was thought that some constituent might have a bearing on the distribution of living organisms, either by its action on an organism itself or indirectly by its effect on the bottom deposits in which certain animals live. The composition of the fresh water entering the tidal stretch was studied during the survey of the upper reaches. In the seaward part of the Estuary the effect of the high concentration of mineral salts in sea water overshadows that of any other natural constituent of the mixed Estuary water.

## TEMPERATURE

Under natural conditions, it is to be expected that the temperature of the mixed water in an estuary will be intermediate between that of the fresh water and sea water at the two ends. In the Tees Estuary, however, large quantities of water in the central reach are pumped out and used for cooling purposes in various industrial processes; the return of this water at a higher temperature affects the temperature of the Estuary waters. Thus, in one works alone, about 4.2 million gallons of water per hour are used for cooling purposes and are raised in temperature by  $7\frac{1}{2}^{\circ}\text{C}$ . The volume of water pumped through this factory in  $2\frac{1}{2}$  days is approximately equal to the volume of the Estuary between Stockton and Newport at mean tide level. In addition to numerous discharges of cooling water, there are effluents of the coke oven type, which are usually discharged at temperatures of 20 to  $30^{\circ}\text{C}$ .

The water in the central reaches of the Estuary is thus normally at a higher temperature than the sea or the upper river. The extent of the difference may be seen from Fig. 16, where the mean temperatures of the upper river at Croft, of the central stretch of the Estuary (salinity 15 to 20 gm. per 1,000 gm.), and of the seaward end (salinity greater than 27 gm. per 1,000 gm.) for the years 1930 and 1931 are shown. The temperatures plotted are the averages of 10 to 30 observations per month in each of the three sections. A typical example of the temperature distribution in the Estuary is shown in Fig. 17, which is drawn from a series of observations made at about the time of high water on 11th October, 1929. The relatively high temperatures in the central stretch must accelerate the decomposition of sewage and organic matter and thus lower the concentration of dissolved oxygen. It is possible that these effects may be of importance in hot weather, when the water temperature rises and the dissolved oxygen concentration falls to about the minimum value necessary to support fish life.

## SUSPENDED MATTER

Only a few determinations of the concentration of suspended matter in the Estuary were made, and the data are insufficient to give more than the order of the concentrations. The highest value recorded was on 23rd July, 1930, when the concentration of suspended matter at Cleveland Shipyard at the surface and at a depth of 1 fathom at low water was 25 parts per 100,000. On the day previous to the determinations there had been a large flood from the upper reaches, the river rising to a height of 11 ft. on the gauge at Croft. The water at Cleveland Shipyard when the samples were taken was unusually turbid and yellow, and the salinity at low water had the low value of 1.8 gm. per 1,000 gm. At low water on 13th January, 1930, the water above Stockton, which was completely fresh, contained 15.7 parts of suspended matter per 100,000; the average height of the upper river at Croft on the previous day was 3 ft. 6 in.



The results of some further determinations are given in Table 12. The values given are the averages of samples taken at different depths ; the concentrations of suspended matter were highest sometimes at the surface and sometimes in the sub-surface layers.

TABLE 12—Concentration of Suspended Matter in the Estuary

Height of river at Croft on preceding day.  Ft. in.	Position.	Number of determinations.	State of tide.	Average weight of suspended matter.  Parts per 100,000.
1 6	Transporter Bridge	4	2 hrs. after low water.	0·6
1 9	"	4	L.W.	2·8
2 10	"	1	L.W.	5·2
6 0	"	1	L.W.	3·5
3 2	"	3	H.W.	0·5
1 6	Newport	4	2 hrs. after low water.	6·5
3 2	"	4		1·7
2 6	Stockton	3	H.W.	0·6

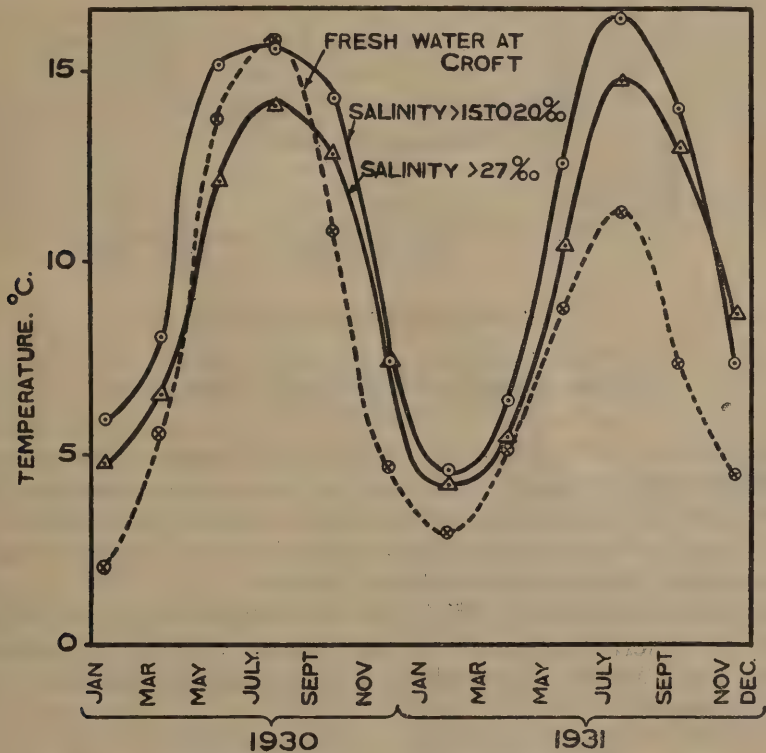


FIG. 16—Temperature of Water at both Ends and in the Centre of the Estuary

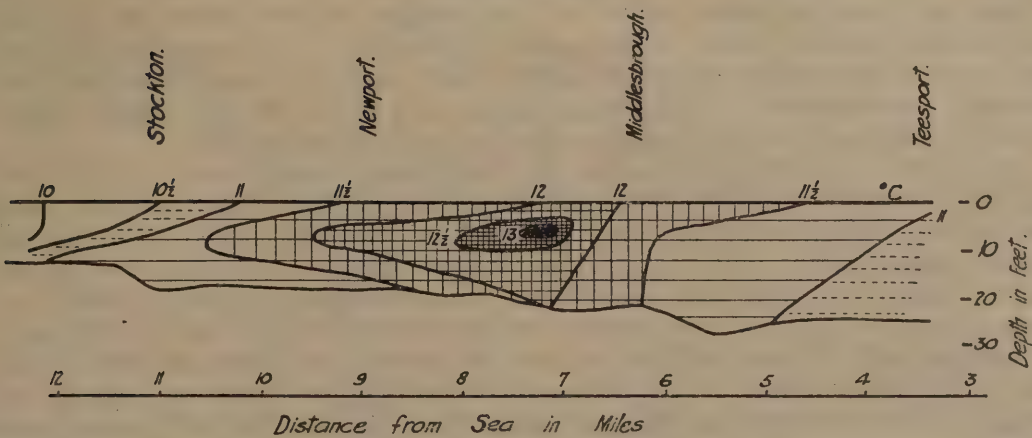


FIG. 17—Temperature of the Tees Estuary at approximately High Water on October 11, 1929

## OPACITY

The extent to which light passes through the waters of the Estuary may have some bearing on the distribution of animals and plants. Several series of observations were made throughout the whole or part of the length of the Estuary, a measure of the opacity being obtained by observing the depth at which it was just possible to see a white plate (Secchi disc) about 1 ft. in diameter. The results obtained are shown graphically in Fig. 18. The depth at which the plate could just be seen in the open water of Tees Bay about 3 miles from the Estuary mouth

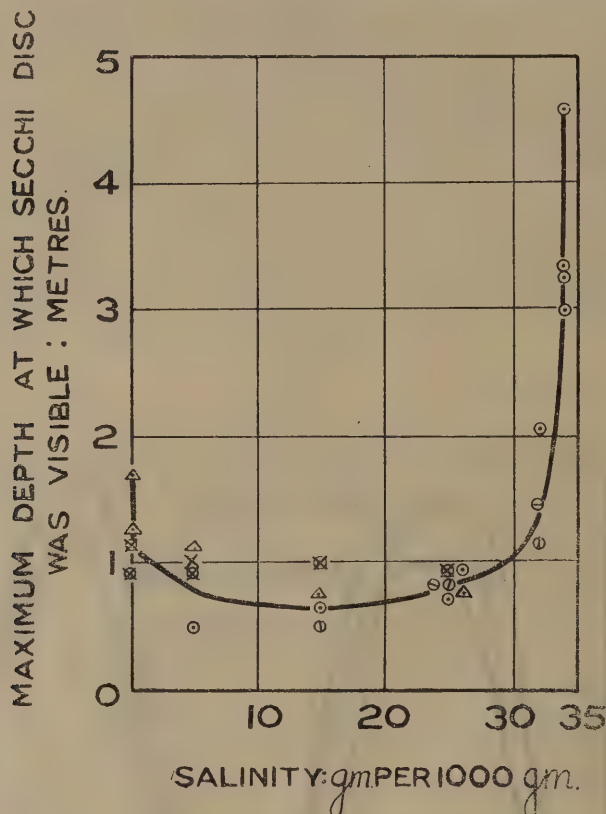


FIG. 18—Opacity and Salinity of the Water in the Tees Estuary

was about  $4\frac{1}{2}$  metres. The opacity increased rapidly as the Estuary was approached and remained nearly constant in the central reaches, falling again somewhat in the stretch of fresh water between Stockton and Yarm. The greater opacity of the water in the central reaches may be due partly to the influence of sewage and industrial effluents discharged into it.

The observations plotted in Fig. 18 were made when the upper reaches contained only a moderate amount of peat colour. When the river is in flood and is washing down peaty material from the upland moors, the opacity may be considerably greater.

## HYDROGEN ION CONCENTRATION

Pure sea water has a hydrogen ion concentration of between  $10^{-8}$  and  $10^{-8.3}$  gm. per litre (pH 8.0 to 8.3)<sup>(1)</sup>. The reaction of the water of the upper Tees is more variable, being influenced considerably by photo-synthesis and by fresh water floods, which may carry acidic peaty material from the upland moors. Normally, the reaction of the river at Yarm is a little on the alkaline side of neutrality, although it may become slightly acid during spates.

In general, the pH of the water in the Estuary was between the values for fresh and sea water, indicating that no appreciable alteration in reaction is brought about by the addition of polluting material or by other causes. Occasionally, however, disturbances which are almost certainly due to the addition of industrial effluents have been recorded. During the months April to June, 1931, the pH values of 300 samples of water taken in the central reaches of the Estuary all lay between pH 6.9 and pH 8.0, except in the case of three samples. One of these had a value as low as 5.8, although other samples drawn on that day were normal. The other two exceptional values were for samples both taken on one day, when apparently about 1 mile of the Estuary had the very low pH value



of 2·8. These are the only occasions when pH values below 6·5 were observed in the general body of the Estuary waters. In some cases the water in the central reaches had a pH value greater than 6·5, but was more acid than that at the ends of the Estuary. Thus, on 13th September, 1929, a series of samples was taken along the Estuary at a depth of 1 fathom and the results given in Table 13 were obtained.

TABLE 13—*pH Values of Samples of Estuary Water taken on 13th September, 1929*

Salinity range. Gm. per 1,000 gm.	Average pH.	Number of determinations.
0	8·0	1
0- 5	7·8	3
5-10	7·5	1
10-15	7·4	2
15-20	7·4	9
20-25	7·3	4
25-27·5	7·6	5
>27·5	7·9	1

Extreme pH values while not as a rule found in the general body of the Estuary waters, were frequently recorded in the neighbourhood of discharges of certain industrial effluents. The effluents from the coke ovens usually have a fairly constant flow, but the discharge of spent pickle liquor from galvanizing works is usually intermittent. The liquor may contain from 3 to 17 per cent. of free hydrochloric acid, and it seems probable that the low pH values occasionally recorded in the central part of the Estuary were found when there had been a discharge of spent pickle liquor immediately before the samples were taken.

#### EXCESS BASE

Sea water contains a concentration of bases in excess of the equivalent concentration of stable acid radicals, the remaining "alkali reserve" or "excess base" being in combination with carbonic acid. The concentration of excess base normally varies in sea water from 0·0023 to 0·0026 normal<sup>(1)</sup>. In the upper river the concentration of excess base is lower in times of spate than under dry weather conditions. Three series of samples taken throughout the Estuary were examined and the results are given in Table 14. In two of the series the concentrations in the central reaches were intermediate between those at the ends. On the third occasion, on 13th September, 1929, the concentration of excess base in the central reaches was lower than in the fresh water reaches and in water of high salinity at the Estuary mouth. The third series of results was from the same samples as were used in the determinations of hydrogen ion concentration shown in Table 13. Both pH values and the data in Table 14 indicate a discharge of an acid effluent into the central reaches of the Estuary.

TABLE 14—*Concentrations of Excess Base in the Estuary on 4th, 9th, and 13th September, 1929*

Salinity range. Gm. per 1,000 gm.	Excess Base : Average normality.		
	4th September, 1929.	9th September, 1929.	13th September, 1929.
0- 5	0·0008	—	0·0023
5-10	0·0016	—	0·0022
10-15	0·0017	0·0017	0·0021
15-20	0·0018	0·0018	0·0020
20-25	0·0020	0·0020	0·0021
25-30	0·0021	0·0020	0·0023
> 30	0·0022	0·0020	—

PHOSPHATES AND IRON

Since domestic sewage contains a considerable concentration of phosphates it was thought that a knowledge of the distribution of phosphate in the Estuary might serve as an index of the distribution of sewage. Seven series of samples were taken during April and May, 1929, throughout the length of the Estuary; the results of determinations of phosphates in solution are given in Table 15.

TABLE 15—Concentrations of Dissolved Phosphate in the Estuary Water

Date.	Number of determinations.	Concentration of $P_2O_5$ Parts per 100,000.	
		Maximum.	Minimum.
18.4.29	22	5	1
19.4.29	19	6	1
22.4.29	6	4	2
23.4.29	22	8	1
24.4.29	25	6	1
25.4.29	23	4	1
2.5.29	19	4	1

These values are of the same order as those found in the open waters of the North Sea. Thus, the maximum and minimum concentrations observed in samples taken from four positions in the North Sea in the month of April were 4 and 3·5 parts per 100,000 respectively<sup>(2)</sup>. Concentrations ranging from 0·3 to 3·5 parts  $P_2O_5$  per 100,000 have been reported for the waters of Plymouth Sound<sup>(3)</sup>. A concentration of 14·2 parts  $P_2O_5$  per 100,000 was observed in the polluted section of the Skerne in February, and 6·3 parts per 100,000 at a station below the junction of the Skerne and the Tees.

In the Estuary the phosphate appeared to be irregularly distributed, the maximum concentration being found in different stretches at different times. It is probable that some of the phosphate of sewage is precipitated as ferric phosphate, since besides the iron in the sewage itself, iron salts containing about 15,000 lb. of iron are discharged daily into the Estuary as constituents of spent pickle liquor. About 2 per cent. of the total iron is in the ferric condition, and 98 per cent in the form of ferrous chloride. In no case have soluble ferrous or ferric salts been detected in the general body of the Estuary water, but insoluble ferric compounds are usually present in high concentrations. The data in Table 16 refer to samples from which the suspended matter was filtered and dissolved in hot hydrochloric acid and ferric iron determined in the resulting solution.

TABLE 16—Concentrations of Insoluble Ferric Iron in the Estuary

Date.	Number of determinations.	Insoluble Ferric Iron. Parts per 100,000.		
		Maximum.	Minimum.	Mean.
8.7.29	51	250	30	110
10.7.29	34	340	60	165
16.7.29	50	700	60	151
24.7.29	16	460	60	237
1.8.29	19	600	60	201



In a few samples containing high concentrations of iron the phosphate content of the suspended matter was also determined and the results are given in Table 17. It appears from these data that the phosphate discharged into the Estuary is partially precipitated, the concentrations of soluble phosphate being thus lowered. Under these conditions it is impossible to estimate the distribution of sewage material in the Estuary from the distribution of soluble phosphates.

TABLE 17—*Concentrations of Insoluble Iron and Phosphate in Samples of Estuary Water*

$P_2O_5$ Parts per 100,000.	Fe Parts per 100,000.	Percentage of total Fe present as $FePO_4$ .
13	340	1.5
20	460	1.7
72	900	3.2
64	850	3.0
60	800	3.0

#### CONSTITUENTS OF INDUSTRIAL EFFLUENTS

Industrial effluents arising from the treatment of coke oven or other coal gas contain, generally, a complex mixture of substances, the exact nature of which is in many cases unknown. During the survey the industrial effluents were first examined, and their constituents or groups of constituents which are most toxic to animal life were identified. The distribution of these substances in the Estuary water was then investigated under different tidal and fresh water conditions. An account of the distribution of these directly poisonous substances is given in Chapter XIV, where the factors leading to the death of fish in the Estuary are discussed. Here it is necessary only to mention the general order of concentrations found.

Sulphides are discharged in considerable quantities as constituents both of spent still liquors and of effluents resulting from the cooling of coke oven gas by direct contact with Estuary water. In the latter type of effluent their concentration varies widely and may be as high as 20 parts per 100,000. Soluble sulphides were not however detected in the general body of the Estuary water. It is probable that they are precipitated, largely as iron sulphide.

The group of monohydric and higher phenolic substances known collectively as "tar acids" is contained both in spent still liquors and in effluents arising from the cooling of gas by direct contact with Estuary water. Near the outfalls of these effluents high concentrations of tar acids were found. In the centre of the Estuary tar acids were usually present in concentrations of the order of 0.01 to 0.02 part per 100,000. The concentrations observed in 396 samples taken during the survey are shown in Table 18. The maximum concentration observed was 0.07 part per

TABLE 18—*Concentrations of Tar Acids in Estuary Water*

Tar acids. Parts per 100,000.	Number of samples.
0-0.01	280
0.01-0.02	85
0.02-0.03	19
0.03-0.04	5
0.04-0.05	3
>0.05	4

100,000 on two occasions. The highest concentrations of tar acids, as of other polluting substances, were found in the central reaches of the Estuary, where

the water was a mixture of roughly half sea water and half fresh water. Table 19 is prepared from the same data as Table 18.

TABLE 19—*Concentrations of Tar Acids in Waters of Different Salinity*

Salinity range. Gm. per 1,000 gm.	Average concentration of tar acids. Parts per 100,000.
0- 7	0.006
7-14	0.012
14-21	0.010
21-28	0.005
28-35	0.004

Effluents from gas coolers in which coke oven gas is cooled by direct contact with Estuary water contain cyanide. This is the most toxic substance discharged into the Estuary; its distribution is discussed in Chapter XIV. The concentrations found in 248 samples examined during the months April to June, 1931, are shown in Table 20. These concentrations are probably considerably lower than the true values owing to the limitations of the methods of determination available (see Appendix I).

TABLE 20—*Concentrations of Cyanide in Estuary Water*

Parts (CN) per 100,000.	Number of samples.
0	84
0.002	37
0.003-0.004	45
0.005-0.006	32
0.007-0.008	15
0.009-0.010	12
>0.010	23

#### REFERENCES

- <sup>(1)</sup> HARVEY, H. W. *Biological Chemistry and Physics of Sea Water*. Cambridge University Press, 1928.  
<sup>(2)</sup> ATKINS, W. R. G. *J. Mar. biol. Ass. U.K.*, 1923, **13**, 136.  
<sup>(3)</sup> ATKINS, cited by HARVEY, H. W., see <sup>(1)</sup> above, p. 174.



## CHAPTER VI

## THE BED OF THE ESTUARY

In the reaches of the Estuary between Yarm and Stockton the bottom consists of uncovered shelves of rock, or of deposits of gravel and clay. The bottom is, on the whole, natural, and is not disturbed by dredging except in certain reaches where gravel is obtained commercially on a relatively small scale. Below Stockton the bottom deposits, which consist at first of a stiff clay, become softer, until in the central reaches of the Estuary large areas of the bottom and foreshore are covered with a soft, glutinous, black mud. Below Cargo Fleet, the mud in the dredged channel is gradually replaced by sand, the seaward limit of the mud belt depending largely on the amount of dredging carried on in these reaches. On the flat areas on both sides of the channel, however, the mud persists for a much greater distance, especially on the Seal Sands on the north bank where there is thick mud as far as the Seaton Channel. The nature of the deposit in this part of the Estuary evidently depends on the strength of the tidal current, and the flat areas on the banks, bounded by training walls at the sides of the main channel, act as lagoons where the finer material is deposited.

The character of the bottom and foreshore deposits has a marked influence on the types of organisms found in an estuary, and an attempt was made to discover some correlation between the composition of the deposits and the rather irregular occurrence of certain mud-burrowing animals living in them. The muddy deposits in the central part of the Estuary contain organic matter which is continuously being decomposed by bacterial action, the rate of decomposition increasing as the temperature rises. In warm weather innumerable bubbles of gas may be seen breaking at the surface of the water in the reaches between Newport and Middlesbrough. If the mud at the bottom is disturbed and the gas which rises to the surface collected, it is found to be inflammable. The evolution of gas containing inflammable hydrocarbons results from the decomposition of organic matter, and its occurrence in marshes and muddy swamps is well known. The decomposition of the Estuary mud when covered with water is brought about partly by anaerobic processes and partly as the result of oxidation processes, oxygen being absorbed from solution in the water. The bottom deposits constitute a reservoir of oxidisable material, to which organic matter, either brought in from the upper reaches or discharged in sewage and industrial effluents, is continuously being added. While the deposits are built up throughout the whole year, their decomposition occurs mainly when the water temperature is high. The oxidation of the organic material which enters the Estuary is thus at a maximum in the summer months, when dissolved oxygen from the Estuary waters is used in the oxidation both of the suspended and soluble material entering from day to day and of the deposited matter which has accumulated throughout the winter.

The factors which determine the suitability of mud as a habitat for different species of burrowing animals are not accurately known. In the Estuary, besides the variations which normally occur in the consistency and composition of "natural" deposits, it is possible that the mud may contain directly poisonous material derived from industrial effluents. Substances which might be poisonous to burrowing animals include tarry and oily material, which can be seen in the mud in certain places in the Estuary particularly near the outfalls of coke oven effluents; the mud near these outfalls contains no animals. Some estimations of the concentration of oily and tarry matter soluble in petroleum ether and benzol were carried out on samples of mud taken from positions near the centre line of the Estuary, and the numbers of burrowing animals per unit area of this mud were also observed. The general character of the bottom deposits in different parts of the Estuary was determined from chemical examination.

## MOISTURE, ORGANIC MATTER, NITROGEN AND OXYGEN ABSORPTION

In general, the soft glutinous muds which were left uncovered by the tide in the central part of the Estuary had a high water content and high concentrations

of organic and nitrogenous matter. The relations between the moisture content of samples of mud from the shore between Yarm and the sea and their content of nitrogen, organic matter and biologically oxidisable material are shown in Fig. 19. In samples dug from the foreshore or taken from the bottom in a special apparatus (Chapter IX) it is impossible to avoid taking up some adventitious water with the mud. This was allowed to drain away before the moisture content of the mud was determined. The diagrams indicate that the soft, glutinous muds of high moisture content contain the highest concentrations of nitrogen and of oxidisable organic matter. The relation between the proportion of nitrogen and loss on ignition in a number of samples is also shown in Fig. 19. The samples from which

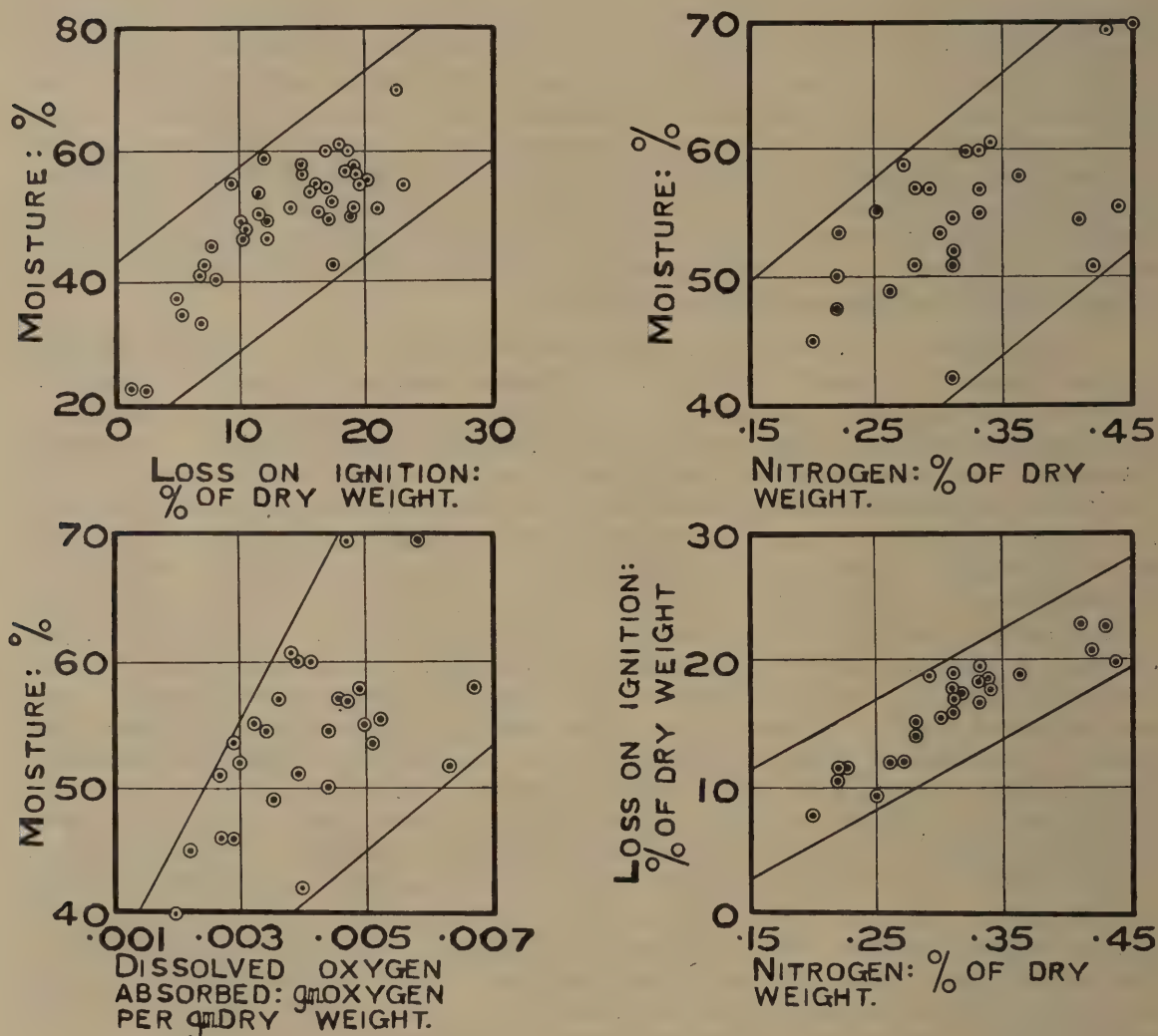


FIG. 19—Relative Concentrations of Various Constituents of Mud from the Tees Estuary

the data used in the construction of Fig. 19 were obtained were taken either from the bottom of the Estuary at least 30 yards from the shore or from the foreshore at positions outside the immediate influence of discharges of sewage or industrial effluents. No detailed examination was made of the mud in the neighbourhood of these outfalls, but there is evidence that below discharges of coke oven effluents the mud contained very high concentrations of organic matter consisting largely of tarry substances. For example, a sample taken from the foreshore about 8 yards below the point of discharge of an effluent from a series of coke oven gas coolers had the following composition: moisture, 65 per cent.; loss on ignition, 33.2 per cent. of dry weight; nitrogen, 0.07 per cent. of dry weight. The dried mud was tarry in appearance and was inflammable. The distance from a given outfall to which this type of mud extended is not known, but there were several stretches of foreshore of about 50 yards in length where black, tarry deposits occurred. The change in the character of the mud throughout the Estuary is



illustrated in Fig. 20, where the losses on ignition of samples taken between the mouth of the river Leven and Fifth Buoy Lighthouse, a distance of about 16½ miles are shown. The soft muds, with a high loss on ignition and high contents of nitrogen and moisture, were found mainly in the central reaches.

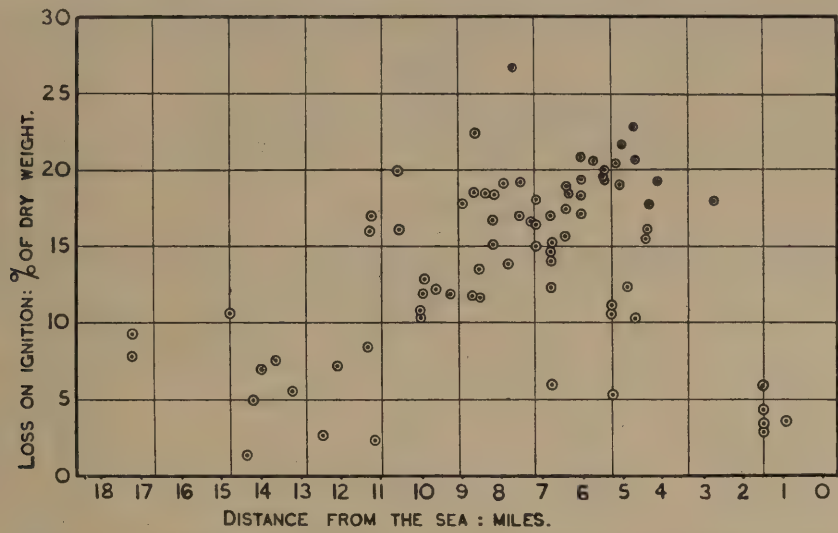


FIG. 20—Composition of Mud from the Foreshore and Bottom in the Tees Estuary

A sample of mud from the Tees, just above its junction with the Leven, and two samples from the Estuary of the Tay, had the compositions given in Table 21.

TABLE 21—Composition of Samples of Mud from the Estuaries of the Rivers Tees and Tay

Position.	Moisture. Per cent.	Loss on ignition. Per cent. of dry weight.	Nitrogen. Per cent. of dry weight.	Oxygen absorbed in 5 days at 18.3° C. Gm. per gm. dry weight.
Mouth of Leven (Tees)...	55	9.3	0.25	0.0032
Carey (Tay). Corresponding with position of Leven mouth in the Tees	64	11.8	0.13	0.0032
Birkhill (Tay). Corresponding with position of Newport in the Tees.	34	4.2	0.08	0.0012

The Tees, at its junction with the Leven, although receiving a small quantity of sewage from Yarm, is not heavily polluted. The Tay receives a very small volume of sewage about 2 miles above the corresponding position at Carey, at which, however, it is relatively unpolluted.

SUBSTANCES SOLUBLE IN PETROLEUM ETHER AND BENZOL

A few determinations of the concentration of substances soluble in petroleum ether and in benzol were made on a series of samples from the Estuary bottom and quantitative estimations of the living organisms in these samples were carried out at the same time. The dried mud was first extracted with petroleum ether and later with benzol. The first extract had an oily appearance; the extract with benzol was dark coloured and apparently consisted of tarry material. The composition of the soluble substances extracted is unknown but the method was

employed with the object of obtaining information on the variation in the concentration of polluting material in mud from different parts of the Estuary. The results are given in Table 22.

TABLE 22—*Substances Soluble in Petroleum Ether and Benzol in Mud from the Tees Estuary*

Amounts as percentages of dry weight  
Number of determinations in brackets

	Position of sample.					Maximum observed concentra- tion.
	Stockton to Newport.	Newport to Furness Cut.	Furness Cut to Cargo Fleet.	Cargo Fleet to Tees Port.	Seal Sands.	
Petroleum Ether.	0.41 (4)	0.45 (8)	0.52 (5)	0.40 (4)	0.16 (2)	0.85
Benzol.	0.29 (4)	0.36 (8)	0.33 (5)	0.27 (4)	0.12 (2)	0.58
Total	0.70 (4)	0.81 (8)	0.85 (5)	0.67 (4)	0.28 (2)	—

The quantity of substances dissolved was, in general, highest from the soft glutinous muds in the central reaches of the Estuary, falling to a comparatively low value in the mud of the Seal Sands which are further from the sources of industrial pollution. The variations in the number of animals in the samples examined are discussed in Chapter IX.

It was considered possible that substances toxic to fish or other animals might be dissolved out of mud in contact with water. About 15 litres of tap water were allowed to remain for two weeks at a temperature of about 20° C. in contact with mud taken from the foreshore opposite the Cleveland Shipyard. The water at the end of this period was non-toxic to trout.

SALINITY OF WATER RETAINED IN THE MUDDY FORESHORE

It has been shown by Reid<sup>(1)</sup> that the salinity of the water retained in a sandy foreshore at low water may be considerably higher than that of a stream of brackish water flowing over it. A few similar observations were made on the salinity of the water held in the muddy foreshore of the Tees Estuary<sup>(2)</sup>, when exposed at low water.

At low water a small hole, some 6 in. deep, was dug in the mud about 3 ft. from the water's edge, and the water which slowly percolated into it was removed by a pipette and filtered. A sample of Estuary water was taken at the same time a few feet off-shore and the salinities of both samples were determined. The results are shown in Table 23 which also includes the average salinity at high water near the Estuary bottom opposite the positions of sampling. The salinity of the water contained in the mud was in all cases considerably higher than that of the Estuary water at the same time and position.

TABLE 23—*Salinity of Water Retained in the Muddy Foreshore of the Tees Estuary*

Distance from sea.	Salinity of water in mud at low tide.	Salinity of water off-shore at low tide.	Average salinity of water near the bottom at high tide.
Miles.	Gm. per 1,000 gm.	Gm. per 1,000 gm.	Gm. per 1,000 gm.
6	28.4	12.6	30.0
6	22.3	14.2	30.0
10	11.5	0.0	25.0
11½	5.0	0.0	21.0



In Table 24 is shown the salinity of the water retained in the muddy foreshore opposite Cleveland Shipyard and the extent of its change as the ebb tide receded and a wider belt of mud was exposed.

There was no appreciable change in the salinity of the water in the mud while it was uncovered during the ebb. It will be noticed that the salinity of the entrapped water in the sample of mud taken at low water about 1 ft. from the water's edge was considerably higher than that of the Estuary water which had covered it only a few minutes before. The bottom and foreshore deposits constitute a medium in which the salinity, compared with that of the Estuary water, remains relatively constant, a factor which is of considerable importance in the distribution of living organisms in the Estuary.

TABLE 24—*Change of Salinity of Water Retained in the Muddy Foreshore at Cleveland Shipyard During the Ebb*

Hours before low water.	Salinity of water in mud. Gm. per 1,000 gm.					Salinity of water off-shore.
	Distance from low water mark.					Gm. per 1,000 gm.
	22 ft.	16 ft.	11 ft.	6 ft.	1 ft.	
1½	21·8	—	—	—	—	18·9
1¼	—	21·6	—	—	—	—
1	22·9	22·2	21·6	—	—	17·9
¾	22·4	22·0	21·8	18·4	—	16·2
0	22·9	22·2	22·2	23·1	23·2	12·7

REFERENCES

<sup>(1)</sup> REID, D. M. *J. Mar. biol. Ass. U.K.*, 1930, 16, 609.  
<sup>(2)</sup> ALEXANDER, W. B., SOUTHGATE, B. A., and BASSINDALE, R. *J. Mar. biol. Ass. U.K.*, 1932, 18, 297.

## CHAPTER VII

## FLORA AND FAUNA

In considering the fauna and flora of the Tees Estuary the stretch from Yarm to the sea was arbitrarily divided for purposes of reference into thirteen sections, numbered I to XIII, each approximately  $1\frac{1}{2}$  miles in length. The channel to the north of Seal Sands (Greatham Creek and the Seaton Channel) was divided into two sections, numbered S XI and S XII. These sections are shown in Fig. 21.

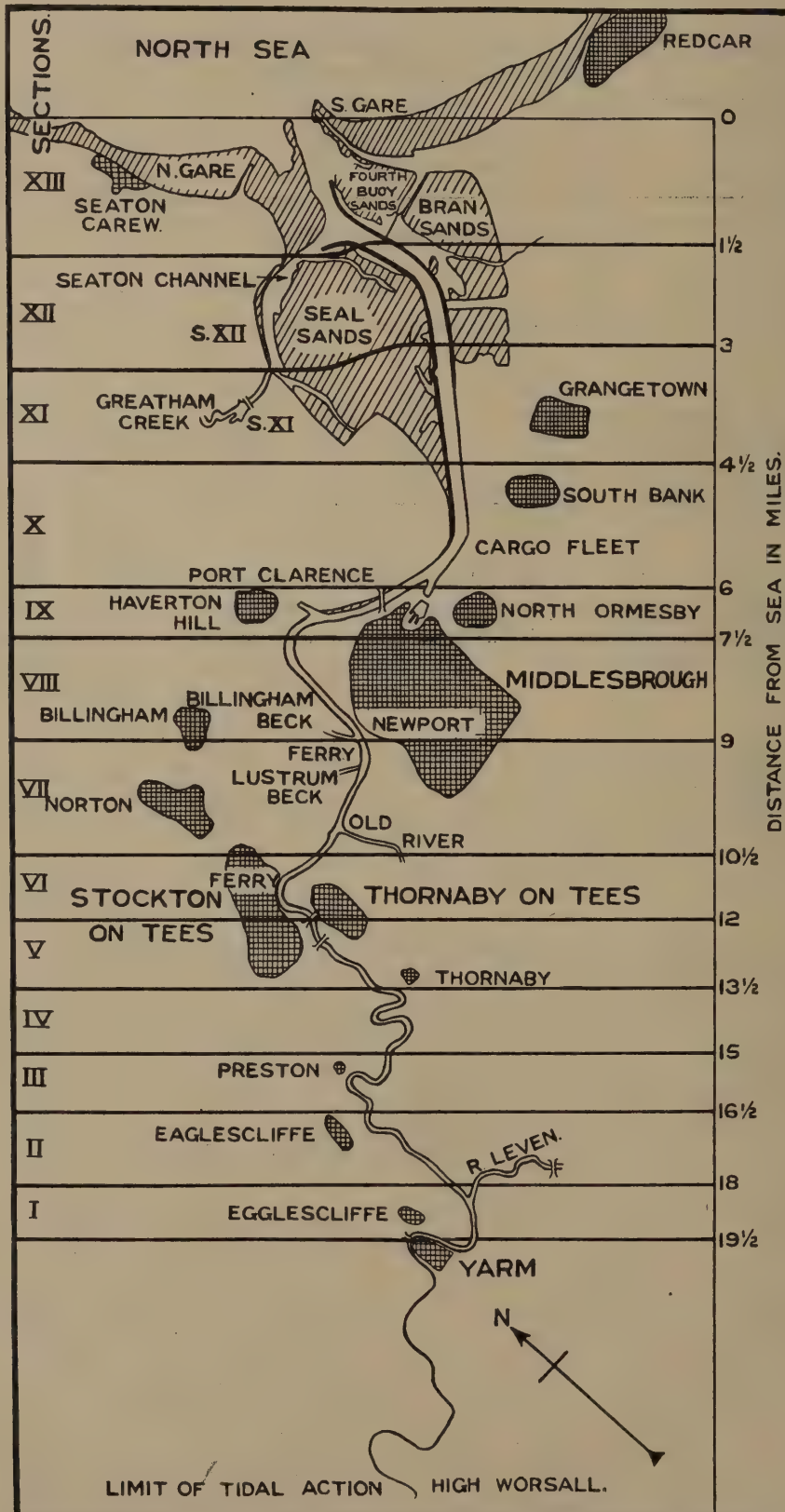


FIG. 21—Diagram of Tees Estuary showing Division into Sections for Biological Survey.



Collections from the shore at low water were made by hand, and those from the bed of the Estuary by means of a small river dredge and a shrimp trawl. Samples of the bottom deposits for examination were collected by means of the apparatus described by Moore and Neill<sup>(1)</sup>, except that the glass tube ordinarily inserted in the outer brass tube was omitted. For collections of plankton, tow-nets of medium and fine mesh were employed. Attention was directed mainly to organisms which are attached or have no great power of movement. Except for planktonic organisms, microscopic species were not identified. Only plants which are wholly aquatic were included.

The fauna and flora at the mouth were typical of a sea shore and at the head of the Estuary the organisms were similar to those found in the non-tidal part of the river. A few brackish water species were observed in the central reaches, whilst certain euryhaline and migratory fish were found throughout the Estuary. In the upper part (Sections I to V) the banks are steep and consist of either earth or slag. The bottom is rocky with patches of sand and gravel, affording a suitable habitat for animals and plants which are attached or for animals which live under stones. From Section VI to X the banks are mainly of slag, in many places lined with wharves and providing attachment for intertidal plants and sessile animals. Mud-burrowing animals live in the muddy bottom and in the intertidal patches of mud. Below Section X the bottom consists of sand and rock, and animals which live on a sandy or rocky bottom become common. The slag training walls provide a habitat for sea weeds and rock-living animals, whilst extensive flats of sand and mud behind the walls form a varied habitat for burrowing species.

In the following lists the normal habitats, marine, brackish, or fresh water, of the various species are given, together with the sections in the Estuary of the Tees in which the species were found. Unless otherwise stated the Roman numerals in the lists refer to the sections of the Tees Estuary. For purposes of comparison the results are also included of a similar survey of the estuary of the Tay, which is described in more detail in Chapter VIII. The arbitrary division of the Estuary of the Tay into sections is shown in Fig. 25.

The names of marine invertebrate animals are those used in the Plymouth Fauna list<sup>(2)</sup>, and the names of marine plants are from Newton<sup>(3)</sup>, except where otherwise stated. Planktonic diatoms are named from Lebour<sup>(4)</sup>. Most of the fresh-water animals were identified by Mr. F. T. K. Pentelow, and the main authorities consulted were "Die Süßwasserfauna Deutschlands,"<sup>(5)</sup> "Les Larves et Nymphes Aquatiques des Insectes d'Europe,"<sup>(6)</sup> "Die Tierwelt Mitteleuropas,"<sup>(7)</sup> and "Die Tierwelt Deutschlands."<sup>(8)</sup> Fresh water algae are named from West and Fritsch<sup>(9)</sup>, and the higher plants from Bentham and Hooker<sup>(10)</sup> and Butcher and Strudwick<sup>(11)</sup>. All the smaller algae, both marine and fresh water, were identified by Dr. R. W. Butcher. In the identification of animals and plants found in the Firth of Tay assistance was given by Mr. J. Ritchie of the Perth Museum. Marine fishes are named as in the Plymouth Fauna list<sup>(2)</sup>, and fresh water species from Tate Regan<sup>(12)</sup>. The names of birds, which were all identified and recorded by Mr. W. B. Alexander, are those given by Witherby<sup>(13)</sup>.

## FLORA

### CHLOROPHYCEAE (ISOKONTAE)

*Gonium* sp. Fresh water.

Once in plankton, II.

*Eudorina elegans* Ehrenb. Fresh water.

Very common on two occasions, I to V, and XI. Probably washed down from ponds and ditches.

*Volvox* sp. Fresh water.

Once in plankton during heavy flood, VII.

*Pediastrum* sp. Fresh water.

Occasional, I to V Probably washed down.

*Enteromorpha compressa* Grev. Marine.

Almost continuous on rocks and piles near high water mark, XIII to III and S XII. Tay: XIII to IV.

*Enteromorpha intestinalis* Link. Marine.

With *E. compressa*, XIII, XII, VIII to III, S XII and S XI, rare in X.

In VIII circular patches of *E. intestinalis* were found on slag banks within the radius of the spray from cooling water outflows. The fronds were frilled as described for *E. intestinalis* var. *cornucopiae* Kutz. Tay: between tidemarks, XII, XI, X, VIII, VI and V.

*Enteromorpha ramulosa* Hook. Marine.

Rare between tidemarks, XII. Common, S XI.

*Ulva lactuca* L. Marine.

Rocks between tidemarks, XIII to X, S XII and S XI. Commonest near the mouth. Tay: XIII to VIII and VI.

*Cladophora* sp. Fresh water.

Between tide marks and on bottom, I. Rare, II, VI and VIII.

*Cladophora lanosa* Kutz var. *uncialis* Thur. Marine.

Rare, XIII and XII.

*Oedogonium* sp. Fresh water.

Occasional in plankton, I to IX.

*Spirogyra* sp. Fresh water.

Once in plankton, VIII.

*Closterium* sp. Fresh water.

Frequent in plankton, I to IX.

*Vaucheria piloboloides* Thur<sup>(14)</sup>. Marine.

A matted growth usually on mud at high water mark, X to I. Commonest during September and October. Though said to be a marine species, it occurs here in water which is always fresh (I and II) and has not been found below X, where the average high water salinity at the surface is about 22 gm. per 1,000 gm. Tay: I, V, VI, and VIII.

#### XANTHOPHYCEAE (HETEROKONTAE)

*Halosphaera viridis* Schmitz. Marine.

Occasional in the plankton as high as VI.

#### BACILLARIALES (DIATOMALES)

*Melosira* sp. Marine.

Occasional in plankton hauls up to VI.

*Paralia sulcata* (Ehr.) Cleve. Marine.

Once in plankton, XII.

*Coscinodiscus* sp. Marine.

Common in plankton up to VI.

*Actinopterychus* sp. Marine.

Common in plankton up to VI.

*Thalassiosira gravida* Cleve. Marine.

Once in plankton, XII.

*Rhizosolenia* sp. Marine.

Occasional in plankton up to IX.

*Chaetoceras* sp. Marine.

Occasionally common in the plankton near the mouth. Taken up to X.

*Biddulphia* sp. Marine.

Common in plankton near the mouth. Found up to VI.

*Navicula* spp.

Fresh water species were frequently found in the plankton above VI and sessile species of this genus also occur between tide marks in the central part of the Estuary.

*Gyrosigma* sp. Marine.

Occasional in plankton up to VII.

*Nitzschia filiformis* W. Smith. Brackish water.

Long filaments on wharves in VI.



## DINOPHYCEAE (PERIDINIAE)

*Peridinium* sp. Marine.

Rare in plankton up to IX.

*Ceratium tripos* O. F. Müller. Marine.

Occasionally common in plankton up to IX.

*Ceratium fusus* (Ehr.) Duj. and *Ceratium furca* (Ehr.) Duj. Marine.

Once in plankton, XII.

## PHAEOPHYCEAE (BROWN SEaweEDS)

*Ectocarpus litoralis* Lyngbye. Marine.

Common on *Fucus vesiculosus* up to X.

*Pilayella litoralis* Kjellm. Marine.

Epiphytic on *Fucus vesiculosus* up to VII. Commonest near the mouth.

On piles and *Fucus*, S XII. Tay: XIII, XII, XI and IX.

*Desmarestia aculeata* Lamour. Marine.

Tay: between tide marks, XIII, XII, and XI. Along the bottom, XIII and XII.

*Desmarestia ligulata* Lamour. Marine.

Common at low spring tide level at the South Gare breakwater, XIII.

*Fucus ceranoides* L. Marine.

Rare between tide marks, XIII. Tay: XI to VII.

*Fucus serratus* L. Marine.

Forms a zone between tide marks below *F. vesiculosus*. Common, XIII and XII. Found in XI. Tay: XI, X and IX.

*Fucus vesiculosus* L. Common Bladderwrack. Marine.

Common between tide marks near the mouth. Up to X the fronds are normal and the distribution continuous. Above X to VII the growth is stunted and irregular, and the fronds lack vesicles. Although not found in VI a few small plants were seen in V and IV in Autumn, 1931, and Spring, 1932. Common in S XII and S XI (see Chapter IX). Tay: XIII to VI.

*Pelvetia canaliculata* Dene. and Thur. Marine.

Tay: Between tide marks, XI to VII.

*Ascophyllum nodosum* Le Jol. Marine.

Occasional plants or patches on rocks between tide marks up to XI. Good growth to the north and north-west of Seal Sands, S XII and S XI. Tay: XI to VIII.

*Laminaria digitata* Lamour. Marine.

Common at low tide level and in pools behind training walls, XIII and XII.

*Laminaria saccharina* Lamour. Marine.

Common, XIII and XII, in similar situations to *L. digitata*. Commoner in XII than *L. digitata*. Tay: XIII, XII, and XI.

*Chorda filum* (L.) Stackh. Marine.

Not common between tide marks, XIII and XII. Tay: XI.

## RHODOPHYCEAE

*Porphyra umbilicalis* J. G. Agardh. Marine.

Rocks between tide marks, XIII, XII and S XI. Tay: XIII to VIII.

*Batrachospermum moniliforme* Roth. Fresh water.

Tay: Between tide marks and on the bottom, I.

*Lemanea fluviatilis* C. Agardh. Fresh water.

Tay: Between tide marks and on the bottom, I.

*Polysiphonia fastigiata*<sup>(15)</sup> Grev. Marine.

Tay: Between tide marks, XI, X, and IX.

*Polysiphonia* sp. Marine.

Rare between tide marks, XIII.

*Gigartina stellata* J. G. Agardh. Marine.

Tay : Between tide marks, XI and X.

*Rhodymenia Palmetta* Grev. Marine.

Tay : Between tide marks, XI, X, and IX.

*Delesseria sanguinea* Lamour. Marine.

In tidal pools. Frequent, XIII. Rare, XII and XI. Tay : Along the bottom, XI and XII. Between tide marks, XI and VIII.

*Membranoptera alata* Kylin. Marine.

Dredged, XIII. Between tide marks, XII. Rare.

*Ceramium rubrum* C. A. Agardh. Marine.

Fairly common between tide marks, XIII and XII.

*Ceramium tenuissimum* J. G. Agardh. Marine.

Rare between tide marks, S XII.

*Ceramium* sp. Marine.

Tay : Bottom, XIII. Between tide marks, XIII, XI, X, and IX.

*Plumaria elegans* Schmitz. Marine.

Rare between tide marks, XIII.

*Ptilota plumosa* C. A. Agardh. Marine.

Between tide marks and along the bottom, XIII. Rare. Tay : Along the bottom, XIII.

#### MYXOPHYCEAE (CYANOPHYCEAE)

*Lyngbya* sp. Fresh water.

On *Fucus vesiculosus*, VIII.

Blue green algae have been observed in Section I and several other places. They probably occur throughout the Estuary between tide marks.

#### SCHIZOMYCETES

Sewage fungus occurred at the mouths of sewers in the central part of the Estuary and consisted mainly of *Beggiatoa alba* Trev. and *Zoogloea ramigera* Itzig or a zoogloid form of the latter.

#### BRYOPHYTA (MOSSES)

*Fontinalis antipyretica* L. Fresh water.

On rocks between tide marks, I to IV. Bottom, I. Tay : Between tide marks and along the bottom, I, II, and III.

*Euryhinchium rusciforme* Milde. Fresh water.

Rocks between tide marks, I, II, and III. Tay : Between tide marks and along the bottom, I to IV.

#### MONOCOTYLEDONAE

*Zostera marina* L. Marine.

Tay : XI and XII.

*Potamogeton crispus* L. Fresh water.

Tay : Between tide marks and along the bottom, I, II, and III.

*Elodea canadensis* Mich. Fresh water.

Tay : Between tide marks and on the bottom, I.

#### DICOTYLEDONAE

*Ranunculus fluitans* Lam. Fresh water.

Tay : Between tide marks and on the bottom, I.

*Myriophyllum spicatum* L. Fresh water.

Tay : Between tide marks and on the bottom, I, II, and III.

*Callitriche stagnalis* Scop. Fresh water.

Tay : Between tide marks, I to IV.

*Callitriche intermedia* Hoffm. Fresh water.

Tay : Between tide marks and on the bottom, III.



## FAUNA

## PROTOZOA

*Distephanus speculum* (Ehr.). Marine.

Once in plankton, XI.

*Vorticellidae*.

Common on the bottom and between tide marks, IV to IX. On pieces of wood, stones, and *Cordylophora* colonies. Occasionally frequent on living specimens of *Eurytemora* in the plankton. Tay : On planktonic copepods, in central parts of the Estuary.

*Zoothamnion* sp.

Between tide marks, IX, XI, and XII.

## PORIFERA (SPONGES)

*Sycon coronatum* (Ell. and Sol.). Marine.

Single specimen dredged, XIII.

*Grantia compressa* (Fabr.). Marine.

Single specimen between tide marks, XII.

*Halichondria panicea* (Pall.). Marine.

The commonest sponge in the Estuary. Between tide marks, XIII, XII and XI. Dredged, XIII and XII. Tay : Dredged, XI and X.

*Axinella firma* (Bowerbank)<sup>(16)</sup>. Marine.

Obtained once from piles, north bank, XII. Not recorded since first described (*Hymeniacedon firmus*) as found at Jersey in 1867.

*Ephydatia fluviatilis* (Linn.). Fresh water.

Rare, I. Tay : On the bottom, I and II. Between tide marks, I, II, and V.

## Sponge spicules.

Triaxon spicules were common on one occasion in the plankton up to X.

## COELENTERATA (HYDROIDS, ANEMONES, ETC.)

*Clava multicornis* (Förskal). Marine.

Rare between tide marks and in the dredge, XIII. Tay : Dredged, IX.

*Cordylophora lacustris* Allman. Brackish water.

Common at low tide level and on the bottom, IV, V, and VI. Poor growth in 1929 and 1930, III. In 1931 colonies found at low tide level, VIII and IX, over five miles below the previous lower limit of distribution. Tay : Between tide marks, IV, V, and VI. On the bottom, V.

*Eudendrium ramosum* (Linn.). Marine.

Rare on the bottom, XIII and XII.

*Tubularia larynx* Ell. and Sol. Marine.

Between tide marks and on the bottom. Frequent, XIII. Common, XII.

Rare on bottom and absent between tide marks, XI.

*Ectopleura dumortieri* (van Ben.). Marine.

Dredged once, XII.

*Halecium halecinum* (Linn.). Marine.

Numerous once in dredge, XIII.

*Campanularia verticillata* (Linn.). Marine.

Dredged twice, XI, and once, XIII.

*Obelia geniculata* (Linn.). Marine.

Numerous once in dredge, XIII. Between tide marks, XII and S XII.

Tay : Bottom, XIII, XII, and IX.

*Laomedea gelatinosa* (Pallas). Marine.

The commonest hydroid of the Estuary. Abundant on rocks, piles, and *Fucus*, XIII to X. Not so common in 1931, X. Dredged, XIII to XI. On the bottom S XII. Between tide marks, S XII and S XI. Dies down in winter. Tay : Between tide marks, IX, VII and VI. Dredged, VII and V.

*Calycella syringa* (Linn.). Marine.

On other hydroids in dredge, XI.

*Lafoea dumosa* (Fleming). Marine.

Dredged, XIII and XI. Between tide marks, XII and XI. Commoner in XII and XI than in XIII.

*Diphasia rosacea* (Linn.). Marine.

Common between tide marks and on the bottom, XIII. Rare on the bottom, XII.

*Dynamena pumila* (Linn.). Marine.

Abundant between tide marks, XIII. Common, XII. Dredged in both sections. Tay : Between tide marks, X and XI. On the bottom, XI.

*Hydrallmania falcata* (Linn.). Marine.

Tay : On the bottom, XII and XIII.

*Sertularia cupressina* (Linn.). Marine.

The commonest hydroid on the bottom. Abundant, XIII and XII. Common, XI and S XII. Between tide marks, XIII and XII.

*Steenstrupia aurata* Forbes. Marine.

In plankton up to VII. Commonest near the mouth. Tay : Plankton, X and IX.

*Cosmetira pilosella* (Forbes). Marine.

One in plankton, XII.

*Aglantha digitale* Hoek. Marine.

In plankton, frequent up to X.

*Aurelia aurita* (Linn.). Marine.

One, dead, X. Ephyrae frequent in plankton up to X and occasional up to VII.

*Alcyonium digitatum* Linn. Marine.

Bottom, XIII.

*Actinia equina* Linn. Marine.

Abundant between tide marks, several colour varieties, XIII. Tay : Between tide marks, X and XI.

*Tealia felina* (Linn.). Marine.

Between tide marks and on the bottom, not common, XIII. Tay : Between tide marks, X.

*Metridium senile* (Linn.) var. *dianthus* (Ellis). Marine.

Common between tide marks, XIII, XII and S XII. Dredged, XIII and XII. White and orange colour varieties.

*Sagartia troglodytes* (Price). Marine.

Common between tide marks, XIII. Less common, XII. Dredged, XII and XI. Tay : Between tide marks, XII, X, and IX.

*Pleurobrachia pileus* (O. F. Müller). Marine.

Frequent in plankton up to V. Commonest near the mouth.

*Beroë cucumis* Fabr. Marine.

Three in plankton, Dec., 1931, VI.

#### PLATYHELMINTHES (FLAT WORMS)

*Procerodes ulvae* (Oersted). Brackish water.

Tay : Where a stream flowed across the shore, VIII.

*Planaria polychroa* O. Schmidt. Fresh water.

Common between tide marks, I and III.

*Planaria* sp. Fresh water.

Tay : Between tide marks and on the bottom, I to III.

*Dendrocoelum lacteum* (O. F. Müller). Fresh water.

Rare between tide marks, I to III. Tay : Between tide marks, I to III and V. On the bottom, I to III.



## NEMERTINI

*Lineus ruber* (Müller) and *Amphiporus lactifloreus* (Johnston). Marine.

Nemertines are not common and the above two species occur between tide marks, XIII and XII. Tay : One species taken between tide marks, XII. Probably *A. lactifloreus*.

## CHAETOGNATHA

*Sagitta* spp. Marine.

In plankton up to V. Commonest near the mouth. Both *S. elegans* Verril and *S. setosa* J. Müller occur, usually together. Sometimes one species is the commoner, sometimes the other.

## ANNELIDA (WORMS)

## Chaetopoda

## POLYCHAETA

*Lepidonotus squamatus* (Linn.). Marine.

Between tide marks, XIII, XII and XI. Commonest near the mouth. Dredged, XII and XI. Tay : Between tide marks, XI.

*Gattyana cirrosa* (Pallas). Marine.

One specimen from a tube of *Lanice conchilega*, XIII.

*Harmothoe imbricata* (Linn.). Marine.

Occasional between tide marks, XIII and XII. Dredged, XII.

*Lagisca extenuata* (Grube). Marine.

Between tide marks, XIII and XII. Frequent at the mouth only.

Polynoid post-larvae. Marine.

Occasional in plankton near the mouth.

*Halosydna gelatinosa* (M. Sars). Marine.

Between tide marks, once, XIII. Tay : XI.

*Phyllodoce maculata* (Linn.). Marine.

Fairly common among rocks between tide marks, XIII and XII.

Rare, S XII. Dredged once, XII.

*Phyllodoce* sp. Marine.

Tay : Between tide marks, XII and X. On the bottom, XII.

*Eulalia bilineata* (Johnston). Marine.

Occasional on the bottom up to IX. Between tide marks, XI.

*Tomopteris helgolandica* Greef. Marine.

In plankton up to VII. Most frequent near the mouth. Never common.

*Autolytus* sp. Marine.

Swimming buds and complete worms occasionally in plankton up to VII. Tay : In plankton, IX.

*Nereis pelagica* Linn. Marine.

Common among rocks between tide marks, XIII. Less common, XII and S XII. Dredged once, XII. Tay : between tide marks, XIII and XI. On the bottom, XII and IX.

*Nereis virens* Sars. Snake-worm. Marine.

Occasional in sandy mud between tide marks, XIII and XII. Commoner in mud, XI, X, IX, and S XI. Common in mud on the bottom, X and IX. Tay : Between tide marks, IX.

*Nereis diversicolor* O. F. Müller. Rag-worm. Marine.

One of the commonest polychaetes of the Estuary. Rare between tide marks, XIII to XI. Abundant in black mud, X to VII. Up to IV in diminishing abundance. Apparently abundant right across Seal Sands to S XII and S XI. Dredged in X and IX. Tay : Between tide marks, IX to VI. Although classified here as a marine species this worm is not found on the coast near Plymouth except where fresh water is present. It should probably be regarded as a brackish water species.

*Nephtys caeca* (O. F. Müller). Marine.

Tay : Between tide marks, XII and XI. On the bottom, XI and VII.

*Nephtys hombergi* Lamarck. Marine.

Common in sand and muddy sand between tide marks, XIII to XI, S XII and S XI. Tay : XIII and XII.

*Scoloplos armiger* (O. F. Müller). Marine.

Common in sand and muddy sand between tide marks, XIII. Less common, XII. Tay : XIII and XII.

*Aonides oxycephala* (Sars). Marine.

One between tide marks in muddy sand, XII.

*Polydora ciliata* (Johnston). Marine.

Builds small mud tubes covering the shore near low tide level. Abundant, IX. Common, X and VIII. Present, XI. Dredged, IX. The larvae are frequently common in the plankton.

*Magelona papillicornis* Fr. Müller. Marine.

Tay : Between tide marks, XI.

*Audouinea tentaculata* (Montagu). Marine.

In coarse sand or gravel, among rocks between tide marks, XIII to XI.

*Ophelia limacina* Rathke. Marine.

Tay : Dredged, XII, X, and IX.

*Ophelia* sp. Marine.

Occasional in sand, XIII and XII.

*Arenicola marina* Linn. Lug-worm. Marine.

Extensive colonies occur in the tidal sand and muddy sand flats, XIII, XII, XI, S XII and S XI. Tay : XII, XI, IX and VIII.

*Pectinaria koreni* Malmgren. Marine.

One in sand between tide marks, XIII. One larva in plankton, XI.

*Amphiteis gunneri* Sars. Marine.

Tay : Between tide marks, XII.

*Amphitrite johnstoni* Malmgren. Marine.

Abundant in a small patch of red gravel associated with *Paphia pullastra*, XII.

*Terebella lapidaria* Linn. Marine.

Frequent among stones between tide marks, XIII and XII and just into XI.

*Lanice conchilega* (Pallas). Marine.

Common in a patch of sand behind 5th Buoy Lighthouse, XIII. Tay : Between tide marks, XII and XI.

*Loimia medusa* (Savigny). Marine.

Tay : A few larvae in the plankton, IX.

*Fabricia sabella* Ehr. Marine.

Builds mud tubes on piles at about half-tide level. Abundant, X. Common, XI and IX. Less common, XII.

*Hydroides norvegica* Gunnerus. Marine.

Rare, XII.

*Pomatoceros triqueter* (Linn.). Marine.

Fairly common on the bottom and between tide marks, XIII and XII. Between tide marks, XI, S XII and S XI. Tay : Between tide marks, XI.

*Spirorbis borealis* Daudin. Marine.

Not common. On *Fucus*, XIII and XII.

Polychaete larvae are abundant in the plankton at times and are present during the greater part of the year. By far the greater number are *Polydora ciliata* and the distribution of these at high and low water is discussed in Chapter X. Other larvae, probably of marine worms, are found occasionally in the plankton near the mouth. Tay : Polychaete larvae in the plankton, X, IX, and VIII.



## OLIGOCHAETA

*Tubifex benedeni* Udekem. Marine.

A mud-living species. Dense patches on the bottom; common between tide marks at half tide level, XI to VIII.

*Tubifex costatus* (Claparède). Marine.

A mud-living species. Dense patches on the bottom, XI to VIII. Between tide marks, XIII to XI.

The very patchy distribution in the Tees of these two species of *Tubifex* is discussed in Chapter IX.

*Tubifex tubifex* O. F. Müller, and *Limnodrilus hoffmeisteri* Claparède. Fresh water.

Fresh water oligochaetes, found under stones and in mud, I to VII, appear to consist of the above-named species although others may occur. In plankton down to IX. Tay: Between tide marks, I and III to V. On the bottom, I and III.

## HIRUDINEA (Leeches).

*Herpobdella atomaria* Carena. Fresh water.

Never common. In varying numbers between tide marks, I to V. Tay: Between tide marks, IV.

*Helobdella stagnalis* Linn. Fresh water.

Common between tide marks in 1931 only, I. Tay: Between tide marks, IV.

*Glossosiphonia complanata* Linn. Fresh water.

Occasional, I, II and III. Tay: Between tide marks, II, III and IV. On the bottom, II and III.

*Hemiclepsis marginata* O. F. Müller. Fresh water.

One specimen of this rare leech obtained between tide marks in 1931, III.

## ROTIFERA

Rotifers have been noticed occasionally in plankton hauls and are doubtless of frequent occurrence.

## PHORONIDEA

*Actinotrocha* larvae. Marine.

Occasional in plankton during autumn, 1931, XII.

## ARTHROPODA

## Crustacea (Crabs, &amp;c.)

*Cladocera*. Fresh water.

Cladocera appear to be washed into the Estuary from ponds and ditches during floods and are taken in the plankton. Several species appear to be present, one of which is *Alona quadrangularis* O. F. Müller.

*Evadne nordmanni* Lovén. Marine.

Occasional in plankton up to IX. Tay: Fairly common up to X.

*Podon intermedius* Lilljeborg. Marine.

Occasional in plankton, XII. Tay: Fairly common up to IX.

## COPEPODA

*Calanus finmarchicus* (Gunnerus). Marine.

In plankton up to X.

*Pseudocalanus elongatus* Boeck. Marine.

Occasional in plankton, XII.

*Centropages* sp. Marine.

In plankton near the mouth.

*Temora longicornis* (O. F. Müller). Marine.

Frequent in plankton up to X.

*Eurytemora affinis* (Poppe).

The brackish water variety (var. *hirundoides* Nordquist) is extremely widespread and abundant. See Chapter X.

*Acartia* spp. Marine.

*A. clausi* Giesbrecht and *A. longiremis* Giesbrecht have been identified. Frequent in plankton up to X.

*Harpacticids*. Marine.

In plankton up to VIII.

*Alteutha depressa* Baird. Marine.

One in plankton, X.

*Tachidius brevicornis* Lilljeborg. Fresh water.

In plankton, I to VI.

*Oithona helgolandica* Claus. Marine.

Fairly frequent in plankton up to VIII.

#### CIRRIPIEDIA (Barnacles)

*Verruca stroemia* (O. F. Müller). Marine.

Fairly common at low spring tide level, XIII and XII. On the bottom, XIII.

*Balanus balanus* (*porcatus*) (Linn.) da Costa. Marine.

Once on *Mytilus edulis*, XIII.

*Balanus crenatus* Bruguière. Marine.

Between tide marks, XI and XII.

*Balanus perforatus* Bruguière. Marine.

Occasional between tide marks, XII.

*Balanus balanoides* (Linn.). Common Acorn Barnacle. Marine.

On rocks and piles between tide marks. Common, XIII, XII and XI. Frequent, X. Occasional, IX and VIII. Fairly common, S XII and S XI. Tay : Up to VIII.

Cirripede nauplii were frequent in plankton to IX ; Tay : In plankton up to VIII. Cypris larvae were found occasionally in plankton up to X. Tay : In plankton up to VIII. Casts were common in plankton near the mouth. Tay : In plankton up to VIII.

#### MALACOSTRACA

##### Cumacea

*Iphinoë trispinosa* (Goodsir). Marine.

Occasional in plankton up to IX.

##### Isopoda

*Eurydice pulchra* Leach. Marine.

Fairly common in plankton, XIII, XII and XI. Tay : In plankton X.

*Limnoria lignorum* (Rathke). Gribble. Marine.

Attacks the wooden piles in XIII, XII, XI and S XII. Commonest on Redcar Jetty, XII (see p. 69).

*Idotea neglecta* G. O. Sars. Marine.

Occasional, XIII, XII and S XII. Tay : Between tide marks, XI. On the bottom, XIII.

*Idotea viridis* Slabber. Marine.

Between tide marks, on the bottom and in plankton, XIII to X and S XII. Tay : Between tide marks, XII to X. On the bottom, XIII and XII.

*Janira maculosa* Leach. Marine.

Dredged once, XII.

*Jaera marina* (Fabricius). Marine.

Common between tide marks up to IX. Tay : Common, XI to VI.

*Ligia oceanica* (Linn.). Sea louse. Marine.

Rare, X and S XII. Tay : XI and IX to VII.

*Armadillidium vulgare* (Latreille). Wood louse. Terrestrial.

Between tide marks, I to V.

*Asellus aquaticus* (Linn.) Olivier. Fresh Water Louse.

Frequent, I to III.



## Amphipoda

*Bathyporeia pelagica* Bate. Marine.

In dirty sand between tide marks, XIII and XII. Tay: On the bottom, VI.

*Haustorius arenarius* (Slabber). Marine.

In sand between tide marks, XIII and XII. Tay: Between tide marks, XIII and VII.

*Iphimedia obesa* Rathke. Marine.

Once in shrimp-trawl, XII.

*Westwoodilla caecula* (Bate). Marine.

Frequent in sand between tide marks, XIII.

*Nototropis swammerdami* (H. Milne-Edwards). Marine.

Common in shrimp-trawl, XIII (Seaton Channel and the North Gare Sands). Tay: Dredged, XIII.

*Cheirocratus sundevalli* (Rathke). Marine.

Once, between tide marks, S XI.

*Melita palmata* (Montagu). Marine.

Tay: One, between tide marks, IV.

*Gammarellus homari* (J. C. Fabricius). Marine.

Tay: One, XII.

*Gammarus pulex* (Linn.) Desmarest. Fresh Water Shrimp.

Common in the upper river. In Estuary only in I, where it is outnumbered by *G. duebeni*. Occasional in plankton down to VII.

*Gammarus marinus* Leach. Marine.

Common. Between tide marks, XIII to X. On the bottom, XIII to XI and S XII. In plankton up to IX. Tay: Between tide marks, XIII to VIII.

*Gammarus locusta* (Linn.). Marine.

Not so common as *G. marinus*. Between tide marks and on the bottom, XIII, XII, S XII and S XI. Dredged, XI. In plankton up to IX. Tay: Abundant between tide marks, XIII to IX.

*Gammarus zaddachi* Sexton<sup>(17)</sup>. Brackish water.

Tay: Between tide marks or on the bottom, I to IV.

*Gammarus duebeni* Lilljeborg. Brackish water.

Abundant between tide marks and on the bottom, II and III. Common, mainly on the bottom, IV. On the bottom, V and VI. Although a brackish water species, it is common in I, where the water is always fresh, and outnumbers the fresh water species *G. pulex*. In plankton down to VII. Tay: Abundant between tide marks, V to X. On the bottom, VI.

*Talitrus saltator* (Montagu). Marine.

Tay: Common near high water mark, XIII to IX.

*Orchestia gammarella* (Pallas). Sand-hopper. Marine.

Tay: Between tide marks, IX.

*Amphithoë rubricata* (Montagu). Marine.

Fairly common between tide marks, XIII. Tay: XI.

*Corophium volutator* (Pallas). Marine.

Not found in the main channel. Abundant between tide marks in muddy sand and firm mud, S XII and S XI. Tay: Between tide marks, VIII to IV. On the bottom, XII, VI, and IV.

*Corophium crassicorne* Bruzelius. Marine.

Occasional on the bottom, in tow-nets or shrimp-trawl, XIII and XII.

*Chelura terebrans* Philippi. Marine.

Associated with *Limnoria lignorum* in piles, XIII.

*Hyperia galba* (Montagu). Marine.

Rare. In plankton, XII.

*Parathemisto oblivia* (Kröyer). Marine.

Once in plankton, XII.

*Caprella linearis* (Linn.). Marine.

Tay: On the bottom, XII.

## Schizopoda. Marine.

Mysids occur quite commonly on the bottom in XIII, XII and S XII, and may be found in XI and S XI. Four species have been identified; of these *Praunus flexuosus* (Müller) is the commonest; *Neomysis vulgaris* (J. V. Thompson) is much less common and *Leptomysis mediterranea* G. O. Sars and *Schystomysis spiritus* Norman are rare. Above XI the two common species have been found up to IV, where they occur only occasionally. They are probably carried up by a suitable tide and fall back on the ebb or soon die.

*Neomysis vulgaris* (J. V. Thompson). Brackish water.

Tay: Between tide marks, XII, VI, and IV. On the bottom, VII and VI.

*Macropsis slabberi* (van Beneden). Marine.

Tay: In shrimp-trawl, VI.

## Decapoda (Crabs and lobsters)

*Pandalus montagui* Leach. Prawn. Marine.

Fairly common on the bottom, XIII, XII and XI.

*Hippolyte varians* Leach. Chameleon Shrimp. Marine.

Two in shrimp-trawl in 1930, XII.

*Spirontocaris pusiola* Kröyer. Marine.

One dredged, XII.

*Crangon vulgaris* Linn. Common Shrimp. Marine.

A very common species on the bottom, XIII, XII and XI. Frequent; X, and on rare occasions as high as IV. Also occurs in S XII and S XI. Tay: Between tide marks, XII and IX to VI. On the bottom, XIII and VII.

*Galathea squamifera* Leach. Squat Lobster. Marine.

Between tide marks, not common, XIII.

*Porcellana longicornis* (Linn.). Marine.

Between tide marks, XIII. Dredged, XII. Tay: On the bottom, XIII.

Zoea larvae, in plankton, X.

*Eupagurus bernhardus* (Linn.). Hermit Crab. Marine.

Occasional small specimens between tide marks and on the bottom, XIII and S XII. Tay: On the bottom, XIII and XII.

*Portunus depurator* (Linn.). Swimming Crab. Marine.

Common in the dredge, XII. Frequent, XIII and XI. One, dead, stranded, 1929, X.

*Carcinus maenas* (Pennant). Shore Crab. Marine.

Very common on the bottom and between tide marks up to X. Common, S XII and S XI. Rare on the bottom above X, but frequent between tide marks up to VII. Small specimens became common during the summer in X, and it seems possible that the population of the central reaches of the Estuary, consisting of small individuals, may be replaced annually from the sea or that those specimens which survive are stunted in growth and remain small. Tay: Between tide marks, XII to VI. On the bottom, XIII to X and VII.

*Cancer pagurus* Linn. Edible Crab. Marine.

Between tide marks. Common, XIII. Frequent, XII.

*Hyas araneus* (Linn.). Spider Crab. Marine.

Fairly common between tide marks and on the bottom, XIII. Tay: On the bottom, XIII.

Zoea larvae of crabs were frequent. Mainly those of *Carcinus maenas*, which were frequent in plankton up to IX. Tay: In plankton, IX. Megalopa larvae were rarer. Probably mainly of *Carcinus maenas*, in plankton, X.

## Pycnogonida

*Endeis spinosus* (Montagu). Marine.

Rare, between tide marks, XIII.

*Pallene brevirostris* Johnston. Marine.

Frequent on bottom and between tide marks, XIII. Tay: On the bottom XII.



**Mites**

Occasional between tide marks at the seaward end.

**Insecta (Insects)**

*Lipura* sp. Terrestrial.

Occasional between tide marks, II and III.

*Tipulid*. Fresh water.

Larvae on the bottom and between tide marks, I.

*Tanytarsus* sp. Fresh water.

Tay : Larvae between tide marks and on the bottom, I.

*Deronectes* sp. Fresh water.

Larvae, I.

*Deronectes elegans* (Panz.). Fresh water.

One adult, I.

*Agabus paludosus* (Fabr.). Fresh water.

Rare, I.

*Agabus* sp. Fresh water.

One larva, I.

*Gyrinus* sp. Fresh water.

One larva, II.

*Latelmis volkmari* (Panz.). Fresh water.

Larvae between tide marks and on the bottom, I.

*Macronychus 4-tuberculatus* Müller. Fresh water.

Larvae between tide marks, I and II.

*Polycentropus* sp. Fresh water.

Larvae between tide marks and on the bottom, I to III. Tay: I to III.

*Hydropsyche* sp. Fresh water.

Larvae common between tide marks and on the bottom, II and III.

Tay : Larvae between tide marks and on the bottom, I.

*Leptocerus* sp. Fresh water.

Larvae between tide marks and on the bottom, I. Tay: Larvae between tide marks and on the bottom, I.

*Limnophilid* sp. Fresh water.

Larva between tide marks, I. Tay: Larvae between tide marks and on the bottom, I.

*Brachycentrus subnubilis* Curt. Fresh water.

Larvae on the bottom, II.

*Lepidostoma hirtum* (Fabr.). Fresh water.

Larvae common between tide marks, I. Tay: Larvae between tide marks and on the bottom, I.

*Goeriniid* spp. Fresh water.

Larvae of two species between tide marks and on the bottom I and II.

Tay : Larvae between tide marks and on the bottom, III.

*Sialis* sp. Fresh water.

One larva, between tide marks, I.

*Corixa* sp. Water Boatman. Fresh water.

An adult living specimen taken two hours before low water, X.

*Corixid*. Fresh water.

Larva, II.

*Aphelocheirus aestivalis* (Fabr.). Fresh water.

I. This species is peculiar in that it occurs nowhere else in the whole river.

*Ecdyonurus* sp. Fresh water.

Larvae fairly common, II. Tay : Larvae between tide marks and on the bottom, I.

*Baetis* sp. Fresh water.

Occasional larvae in plankton above V.

*Ephemera* sp. Fresh water.

Larvae on the bottom, I. Tay : Larvae between tide marks and on the bottom, I and II.

*Coenis* sp. Fresh water.

Larvae between tide marks and on the bottom, I.

*Perla* sp. Fresh water.

Larvae on the bottom and between tide marks, I.

*Leuctra* sp. Fresh water.

Common between tide marks, I.

*Nemura* sp. Fresh water.

Nymphs, II.

*Protonemura* sp. Fresh water.

Tay : Larvae between tide marks and on the bottom, II.

Insect larvae were taken in the plankton in the upper sections of the Estuary, and those taken as far down as IX had probably been washed down.

#### MOLLUSCA

##### Placophora

*Lepidochiton cinereus* (Linn.). Marine.

Two between tide marks, XIII. Tay : Between tide marks, X and XI. On the bottom, XII.

*Tonicella rubra* (Linn.). Marine.

Tay : Dredged, XII.

##### Pelecypoda (Bivalves)

*Anomia ephippium* Linn. Marine.

Occasional. Dredged, XII and XI. Between tide marks, XIII and XII.

*Mytilus edulis* Linn. Common Mussel. Marine.

An abundant bivalve. Along the bottom, XII and XI. Between tide marks, XIII to X. On Seal Sands on projecting stones to S XII and S XI. Tay : On the bottom and between tide marks, XIII to IX.

*Modiolus modiolus* (Linn.). Marine.

Tay : Dredged, XII.

*Montacuta ferruginosa* (Montagu). Marine.

Associated with *Echinocardium cordatum*, XIII.

*Tellina tenuis* da Costa. Marine.

Common in clean sand between tide marks, XIII, XII, S XII and S XI. Tay : Between tide marks, XIII.

*Macoma balthica* (Linn.). Marine.

Not common. In mud and sand between tide marks, XII. Occasional, XI. Tay : Between tide marks, VIII.

*Scrobicularia plana* (da Costa). Marine.

In muddy patches between tide marks, S XII.

*Spisula solida* (Linn.). Marine.

Dredged, XIII. Tay : XIII.

*Paphia* (*Tapes*) *pullastra* (Montagu). Marine.

Common in patches of gravel and stones between tide marks, XII. Obtained, XIII. Abundant in a small patch of coarse gravel with *Amphitrite johnstoni*, XII.

*Cardium edule* Linn. Common Cockle. Marine.

Rare, XII and XI. The remains of an extensive bed to the north of Seal Sands is said to be still present although the cockles are small, S XII. Tay : Between tide marks, XII and XI. Dredged, XII.

*Mya arenaria* Linn. Clam. Marine.

Between tide marks, S XII. Tay : Between tide marks, VIII and VII.



*Hiatella arctica* (Linn.). Marine.

Rare. Dredged, XII.

*Pholas crispata* Linn. Marine.

Two dredged, XII.

### Gastropoda (Periwinkles, &c.)

*Patella vulgata* Linn. Limpet. Marine.

Common on rocks between tide marks at the mouth. Extends up to XI and S XII. Tay : Between tide marks, XI and X.

*Patina pellucida* (Linn.). Marine.

One on Laminaria roots, XII.

*Acmaea testudinalis* (Müller). Marine.

Tay : Dredged, XII.

*Gibbula cineraria* (Linn.). Marine.

Tay : Dredged, XII.

*Hydrobia jenkinsi* Smith. Brackish water.

Common between tide marks, III, IV & V. Common on the bottom, IV. Tay : Between tide marks, II to VI. On the bottom II and III.

*Littorina obtusata* (*littoralis*) <sup>(18)</sup> (Linn.). Marine.

Frequent between tide marks, XIII and XII. Tay : between tide marks, XI, X and IX.

*Littorina saxatilis* (*rudis*) <sup>(19)</sup> (Maton). Marine.

One between tide marks, XIII.

*Littorina littorea* (Linn.). Periwinkle. Marine.

Common between tide marks, XIII to XI. Across Seal Sands on projecting stones to S XII. Rare, S XI. Tay : XIII to IX.

Eggs of this species common in plankton up to X. Found up to VI.

Tay : In plankton, VII.

*Buccinum undatum* (Linn.). Whelk. Marine.

One between tide marks, XII. Tay : Dredged, XII, XI and X.

*Nucella lapillus* (Linn.). Dog Whelk. Marine.

Common between tide marks, XIII. Less common, XII. Tay : Between tide marks, XII, XI and X.

*Aeolidia papillosa* (Linn.). Marine.

One, eating *Metridium senile*, S XII.

*Facelina curta* (Alder and Hancock). Marine.

Occasionally between tide marks, XIII and XII.

*Idulia coronata* (Gmelin). Marine.

Dredged occasionally near the mouth. Less common near the upper end of XIII.

*Ancula cristata* (Alder). Marine.

Fairly common between tide marks, XIII.

*Goniodoris nodosa* (Montagu). Marine.

Rare. Between tide marks, XIII and XII. Tay : Dredged, XII.

*Onchidorus fusca* (O. F. Müller). Sea Slug. Marine.

The commonest nudibranch in the Estuary. Common between tide marks, XIII. Spawning, March, 1929. Rare between tide marks and along the bottom, XII and XI. Tay : Between tide marks, X.

*Onchidorus aspera* (Alder and Hancock). Marine.

Between tide marks, XIII.

*Palio lessoni* (d'Orbigny). Marine.

Between tide marks, XIII.

*Archidoris brittanica* (Johnston). Marine.

Fairly common between tide marks, XIII and XII.

*Limnaea peregere* (O. F. Müller). Fresh water.

Common between tide marks, I, II, and III. On the bottom, III.

Tay : Between tide marks, I to IV. On the bottom, I to III.

*Ancylastrum fluviatile* (Müll.). Fresh Water Limpet.

Common between tide marks, I, II, III. Tay : Between tide marks,

I to IV. On the bottom, I to III.

### Cephalopoda (Squids, &c.)

*Alloteuthis subulata* (Lamarck.). Squid. Marine.

Three dead specimens picked up, VIII.

Veliger larvae are common in the plankton and were taken up to VI. They were probably mainly veligers of *Littorina littorea* whose eggs were common, and whose post larvae were also obtained in the plankton.

### BRYOZOA

*Gemellaria loricata* (Linn.). Marine.

Tay : Dredged, XIII.

*Bugula flabellata* J. E. Gray. Marine.

Between tide marks and on the bottom, XIII.

*Flustra foliacea* (Linn.). Marine.

Dredged, XIII. Between tide marks, XII.

*Membranipora pilosa* (Linn.). Marine.

Fairly common between tide marks and on the bottom, XIII, XII and XI. Tay : Between tide marks, XIII and XI to VI. On the bottom, XIII to IX and VII.

*Umbonula verrucosa* (Esper.). Marine.

Between tide marks, XIII, XII and XI.

*Alcyonidium hirsutum* (Fleming). Marine.

Fairly common between tide marks, XIII. Tay : Between tide marks, X and IX. Dredged, XII.

*Flustrella hispida* (Fabricius). Marine.

Rare between tide marks, XIII.

Cyphonautes larvae, occasional in plankton up to X. Tay : X.

### ECHINODERMATA (SEA URCHINS)

*Solaster papposus* (Linn.). Marine.

Tay : Dredged, XIII.

*Henricia sanguinolenta* (O. F. Müller). Marine.

One between tide marks, XIII.

*Asterias rubens* Linn. Marine.

Common between tide marks and on the bottom, XIII, XII, and S XII. Rare, XI. Tay : Dredged, XII and XI. Between tide marks, XII, XI and X.

*Ophiothrix fragilis* (Abildgaard). Marine.

Very common between tide marks. Frequent on the bottom, XIII. Between tide marks, S XII.

*Ophiura albida* Forbes. Marine.

Dredged once, XI.

*Psammechinus miliaris* (Gmelin). Marine.

One dredged, XII.

*Echinus esculentus* Linn. Edible Sea Urchin. Marine.

Between tide marks, XIII.

*Echinocardium cordatum* (Pennant). Heart Urchin. Marine.

Common in a small patch of muddy sand at low spring tide level, XIII.

Echinoplutei and Ophioplutei have been observed on a few occasions in the plankton up to XI.



## TUNICATA (SEA SQUIRTS)

*Polycarpa rustica* (Linn.). Marine.

Dredged, rare, XIII.

*Botryllus schlosseri* (Pallas) var. *typica*. Marine.

Common between tide marks, XIII, XII and S XII.

*Botrylloides leachi* Savigny. Marine.

Between tide marks, XIII.

*Ascidella aspersa* (O. F. Müller). Marine.

One obtained between tide marks, XIII.

*Diplosoma listerianum* (Milne-Edwards) var. *gelatinosum* (Milne-Edwards). Marine.

Between tide marks, XIII and XII.

*Oikopleura* (*dioica* ?) Fol. Marine.

Common in the plankton near the mouth. Found as high as V.

Tay : X and IX.

## VERTEBRATA

## Pisces

## CHONDRICHTHYES

*Lampetra fluviatilis* (Linn.). River Lamprey. Fresh water.

One alive and one dead, IV.

*Acanthias vulgaris* Risso. Piked Dog-fish. Marine.

One by handline, XIII.

*Raja clavata* Linn. Thornback Ray. Marine.

One, very small, stranded, XIII.

## OSTEICHTHYES

*Leuciscus cephalus* Linn. Chub. Fresh water.

One dying specimen rescued from attack by gulls, VII.

*Rutilus rutilus* (Linn.) Roach. Fresh water.

One dead with fungus on its head, IV.

*Phoxinus phoxinus* (Linn.) Minnow. Fresh water

Occasional, IV.

*Clupea harengus* Linn. Herring. Marine.

Common at times off the mouth and said to enter the Estuary.

Larval specimens rare in plankton up to IX. A few, two inches long, picked up dead on July 23, 1931, X.

*Clupea sprattus* Linn. Sprat. Marine.

Enters the Estuary in shoals during the summer. Thousands have been seen dying or dead at various times from XIII at low water up to IX at high water. Dying sprats were seen to come to the surface and swim in circles like dying smolts. Gulls and terns gathered in hundreds to feed on the dying sprats.

*Salmo salar* Linn. Salmon. *Salmotrutta* Linn. Sea-trout.

The adult fish are netted near the mouth as they ascend the river to spawn. They are also fished by rod in the upper river. The numbers taken both by rod and by nets have declined considerably in recent years. Occasional dead adult fish have been found stranded on the banks of the Estuary in X to V. The young fish hatched in the fresh water reaches grow there to the smolt stage (usually in two years) and then descend to the sea during the smolt run in April, May and June. Large numbers are killed by pollution in the Estuary ; an investigation of the cause of mortality and an analysis of the size, age, sex and food of the dead smolts picked up are described in Chapter XIV.

The fresh water variety of *S. trutta* (Brown Trout) was once taken in IV.

*Osmerus operlanus* (Linn.). Smelt or Sparling. Marine.

The sparling was once common. The adult fish ascend estuaries to spawn, and the present scarcity of sparling in the Tees may be judged from the fact that only 25 specimens were taken in IV during six weeks of fishing, although the early part of the period coincided with the middle of the spawning season of this species.

*Anguilla anguilla* (Linn.). Fresh water Eel.

The young stages, or elvers, of this migratory species occur occasionally in different parts of the Estuary. An adult silver eel was picked up dead in VII. The half-grown or yellow eel appears to inhabit the upper part of the Estuary and is common in IV (see Chapter XIV).

*Gasterosteus aculeatus* Linn. Three-spined Stickleback.

A fresh water species capable of living in the sea<sup>(20)</sup>. Common in IV. A high proportion of these estuarine specimens had a well developed tail ridge. Living specimens were taken in I, IV, V, VI, VIII and XIII. Not seen above Yarm.

*Syngnathus acus* Linn. Greater Pipe-fish. Marine.

Occasional, XIII and XII.

*Ammodytes lanceolatus* Lesauvage. Greater Sand-eel. Marine.

In sand, XIII. Once taken in X at low water, where they appeared to be in difficulties.

*Ammodytes tobianus* Linn. Lesser Sand-eel. Marine.

Picked up dead, X.

*Gadus morrhua* Linn. Cod. Marine.

Small specimens (Codling) were hooked, XIII. A specimen 3 in. long was taken in the shrimp trawl, XII.

*Gadus merlangus* Linn. Whiting. Marine.

Commonly fished from the Teesport Wharves (XI) at all states of the tide. Common in XIII. Dead and dying fish occasionally observed in X.

*Gadus virens* Linn. Coal-fish. Marine.

Young specimens common, XIII.

*Onos mustela* (Linn.). Five-bearded Rockling. Marine.

XIII and XII.

*Zoarces viviparus* (Linn.). Viviparous Blenny or Eel-pout. Marine.

Frequent among slag, XII. A female had well developed young on 26th January, 1932.

*Centronotus gunnellus* (Linn.). Gunnel or Butter-fish. Marine.

Fairly common among slag, XIII and XII.

*Trachinus vipera* Cuvier and Valenciennes. Lesser Weever or Sting fish. Marine.

Common on the bottom, XIII.

*Lophius piscatorius* Linn. Angler or Fishing-frog. Marine.

Taken in XIII and XII. Two found stranded on the sands on 6th September, 1929, were attacked by gulls but were alive when seen, XII. One dead and one living specimen were observed stranded, X.

*Gobius (Gobiosculus) pictus* Malm. Painted Goby. Marine.

A single living specimen between tide marks, X.

*Pleuronectes flesus* Linn. Flounder or Black-back.

Young specimens occur in estuaries and rivers. Adult black-backs were common in XIII, and occurred up to XI. Planktonic larvae were obtained occasionally up to VII. Growing stages (mainly 2 to 4 in. long) were abundant in IV (see Chapter XIV). Present above Yarm up to Croft. Said to occur at Piercebridge. Occasional dead specimens picked up, V to X. A 10-in. specimen from V showed two winter rings on its scales.



*Pleuronectes platessa* Linn. Plaice. Marine.

XIII.

*Pleuronectes limanda* Linn. Dab. Marine.

Common, XIII. Two young specimens, 1·9 and 1·5 in. long, taken in November, 1930, X.

*Trigla gurnardus* Linn. Grey Gurnard. Marine.

Common, XIII.

*Agonus cataphractus* (Linn.). Armed Bullhead or Pogge. Marine.

Common in the shrimp-trawl, XIII, and in XII.

*Cyclopterus lumpus* Linn. Lump-sucker or Sea-hen. Marine.

Frequent in salmon nets, XIII and XII.

*Liparis montagui* (Donovan). Montagu's Sea-snail. Marine.

One, XIII.

*Scomber scombrus* Linn. Mackerel. Marine.

Occasionally abundant, XIII.

Fish eggs were observed in the plankton near the mouth and appeared to be mainly those of the sprat (*Clupea sprattus*). In the Tay the egg of *Onos* sp. was taken in X.

Larvae of fish were taken in the plankton only rarely near the mouth. In the Tees, larvae of the herring (*Clupea harengus*) were taken on three occasions (October and January), and the larvae of *Callionymus* sp., a goby and (probably) a wrasse were taken once each. In the Tay the larvae of the herring (*Clupea harengus*) and of *Onos* were taken.

### Aves (Birds)

The Tees Estuary was formerly the resort of immense numbers of aquatic birds, and many of the inhabitants of the district earned a livelihood as fowlers. A hundred years ago Hogg wrote that "The Æstuary of the Tees is the resort of every aquatic bird which frequents the German Ocean." A writer about 1600 recorded that "Neere unto Dobham (the Porte of the Mouth of the Teese) [now called Cargo Fleet] the shore lyes flatt, where a shelf of sand raised above the highe water marke entertaines an infynite number of sea-fowle, which lay theyr Egges heere and there scatterlinglie in such sorte, that in Tyme of Breedinge one can hardly sett his Foote so warylye, that he spoyle not many of theyr Nests."

Almost all the species of waterfowl and wading-birds found in the British Isles have been recorded as occurring on the Tees Estuary. The following notes deal only with species observed during the survey.

#### ALCIDAE (Auks)

*Uria troile* (Linn.). Guillemot.

Frequent at the mouth, XIII, and occurs in XII.

*Alca torda* Linn. Razorbill.

Seen at the mouth.

#### LARIDAE (Terns and Gulls)

*Sterna sandvicensis* Lath. Sandwich Tern.

*Sterna hirundo* Linn. Common Tern.

*Sterna paradisea* Brunn. Arctic Tern.

*Sterna albifrons* Vroeg. Little Tern.

These four species were common on the wider portion of the Estuary during the summer and occasionally ascended as far as Middlesbrough, X. On occasions when sprats were dying in the Estuary the Terns joined the Gulls in pursuit of them, but ordinarily they fed chiefly on fish from the shallow pools and channels among the sand-banks, probably mainly sand-eels.

*Larus argentatus* Pont. Herring Gull.

*Larus ridibundus* Linn. Black-headed Gull.

These two species were present throughout the year in very large numbers. During the spring months adults were rare and the species were represented by immature birds.

*Larus marinus* Linn. Great Black-backed Gull.

A few (usually immature) were always present in the lower Estuary.

*Larus fuscus* Linn. Lesser Black-backed Gull.

Most abundant in spring and autumn, doubtless when migrating to and from their breeding grounds.

*Larus canus* Linn. Common Gull.

Plentiful during the winter. Rare in summer.

*Rissa tridactyla* (Linn.). Kittiwake.

Occasional near the mouth.

The Gulls are undoubtedly very valuable scavengers. The mouth of every sewer is normally marked by a mixed flock. They are quickly attracted by the refuse thrown overboard by ships in the river, and the sand-banks, mud-flats and river-banks are patrolled by them at low tide. They are evidently almost omnivorous, feeding largely on organic refuse and on worms, molluscs, crabs or fish left exposed by the tide. They probably obtain very few, if any, healthy fish in deep water, but capture such as are isolated in small pools on the banks or those which come to the surface when dying. Great flocks of gulls assembled in the lower part of the Estuary when sprats were being killed and in the upper part during the spring when the smolts were dying. Except during the smolt season they were only occasionally seen in the portion of the Estuary between Stockton and Yarm.

#### PHALACROCORACIDAE

*Phalacrocorax carbo* (Linn.). Cormorant.

Common throughout the year in the wider part of the Estuary below Cargo Fleet. These birds appeared to feed chiefly in the deep pools behind the training wall, in Seaton Channel and near the mouth, but they might be seen occasionally in the main channel as high as X and occasional individuals were seen in III and IV.

*Phalacrocorax aristotelis* (Linn.). Shag.

Frequent near the mouth in winter.

#### ANATIDAE (Ducks and Geese)

*Tadorna tadorna* (Linn.). Sheld-duck.

One or two pairs inhabited the area near the mouth throughout the year, and bred nearby.

*Anas crecca* Linn. Teal.

Small flocks occurred occasionally in the lower Estuary and near the mouth of Leven, II.

*Mergus merganser* Linn. Goosander.

Two pairs were seen in XI.

Numerous other species of ducks occurred in the marshes adjoining the Estuary but were not noted on the Estuary itself.

#### RALLIDAE

*Gallinula chloropus* (Linn.). Moorhen.

Frequently seen between Yarm and Stockton.

#### ARDEIDAE

*Ardea cinerea* Linn. Heron.

Occasionally seen on the banks between Yarm and Stockton. The only heronry in the Tees valley is a small one at Gainford.



## CHARADRIIDAE

During the winter the mud-flats and sand-banks of the lower Estuary were frequented by great flocks of waders. The commonest species were :—

- Numenius arquatus* (Linn.). Curlew.  
*Limosa lapponica* (Linn.). Bar-tailed Godwit.  
*Calidris canutus* (Linn.). Knot.  
*Calidris alpina* (Linn.). Dunlin.  
*Crocethia alba* (Pall.). Sanderling.  
*Charadrius hiaticula* Linn. Ringed Plover.

Other species, seen in smaller numbers, chiefly during the spring and autumn periods of passage included :—

- Numenius phaeopus* (Linn.). Whimbrel.  
*Tringa nebularia* Gunn. Greenshank.  
*Calidris ferruginea* (Brünn). Curlew Sandpiper.  
*Arenaria interpres* (Linn.). Turnstone.  
*Haematopus ostralegus* Linn. Oystercatcher.

A few pairs of Ringed Plovers remained throughout the summer and bred on the sand-banks near the mouth. A few Curlews were also present on the lower Estuary throughout the summer but did not breed in the vicinity. .

*Tringa totanus* (Linn.). Redshank.

Bred on the adjoining marshes and occasionally visited the muddy banks of the river between Stockton and Middlesbrough as well as the flats of the lower Estuary.

*Tringa hypoleucos* Linn. Common Sandpiper.

Throughout the summer a few pairs frequented the river banks between Yarm and Stockton, where they doubtless breed. In the autumn this species also visited the lower Estuary.

*Alcedo atthis* Linn. Kingfisher.

Occasionally seen between Yarm and Stockton.

## CORVIDAE

*Corvus frugilegus* Linn. Rook.

Frequently visited the banks of the river between Middlesbrough and Stockton at low tide and competed with gulls and rats in picking up refuse from the sewers, etc., stranded on the mud.

## Mammalia

*Phocaena phocaena* (Linn.). Porpoise.

Porpoises not infrequently enter the mouth of the Tees in small schools, but were not observed during the present survey more than a mile above the entrance. The schools were not seen sufficiently plainly for identification, but presumably they were of this species.

*Phoca vitulina* Linn. Common Seal.

The Seal Sands derive their name from the very large colony of Common Seals (*Phoca vitulina*) which formerly inhabited them.

Mennell and Perkins, in their "Catalogue of the Mammalia of Northumberland and Durham,"<sup>(21)</sup> quote the testimony of a seal-hunter of Seaton Carew that their numbers between 1820 and 1830 were about 1,000 but in 1862 only three survived. "The seals exhibit great dread of the steamboats, which have greatly increased in numbers on the river during the last few years, and at the same time the population in the neighbourhood has increased enormously; to these causes may be attributed the rapid decrease of these animals." Such was the dictum in 1863 of the "enthusiastic hunter" who himself had killed "a large number." Seals still appear in the Tees Estuary, and during 1929 several were reported and at least one shot. During the smolt seasons of 1930, 1931, and 1932 a seal was present in the Estuary at Haverton Hill, about seven miles from the mouth. It was seen as late as August and September.

As long ago as 1829, John Hogg attributed part of the decrease in the numbers of salmon in the Tees to the increase of seals at the mouth<sup>(22)</sup>. There seems to be no evidence, however, that the destruction of the seals led to an increase in the numbers of salmon.

*Lutra vulgaris* Erxleben. Otter.

Recorded by Hogg in 1829 as occasionally caught in the Tees near Stockton. Some probably still occur in the upper part of the Estuary between Stockton and Yarm.

*Mus decumanus* Linn. Brown Rat.

Frequently seen on the banks of the Estuary at low tide.

#### DISTRIBUTION OF SPECIES

The numbers of species found in each section of the Estuary are plotted in Fig. 22, in which the birds, fishes and mammals are omitted. A few species of Crustacea—*Crangon vulgaris* and the mysids—are taken as occurring only in

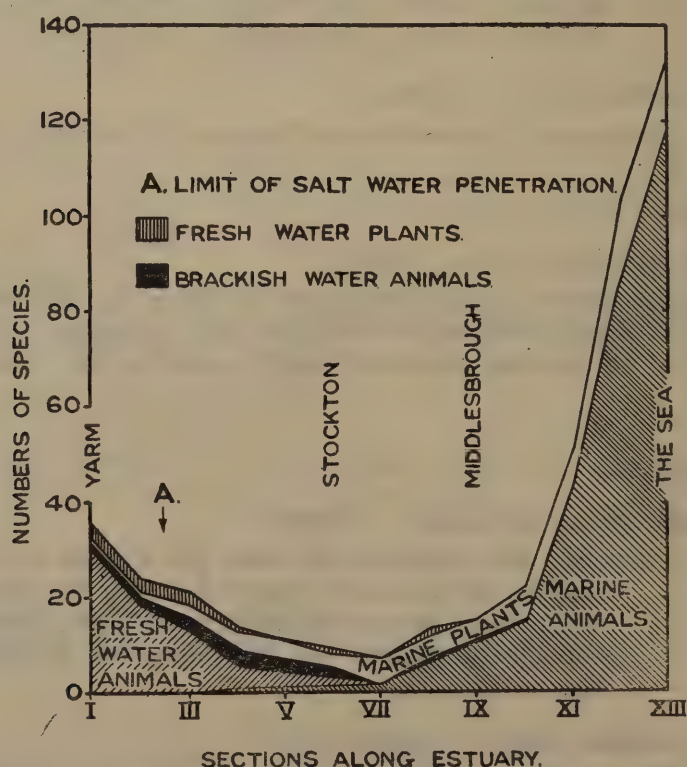


FIG. 22—Composition of the Fauna and Flora along the Tees Estuary



XIII and XII; although these were found on rare occasions and in small numbers up to IV, they were probably carried up by the flood tide and fell back on the ebb. The marine fauna was much more varied than the fresh water fauna and brackish water species were few in number. The most striking feature of the distribution of animals and plants was the dearth of species in the central part of the Estuary. Typical sea-shore fauna and flora at the mouth died away rapidly as the Estuary was ascended and, after passing the central part where few species remained, fresh water species gradually appeared until I the fauna and flora were similar to those found in the non-tidal reaches of the river. Species which live between tide marks were more numerous throughout the Estuary than those always submerged on the bottom (Fig. 23).

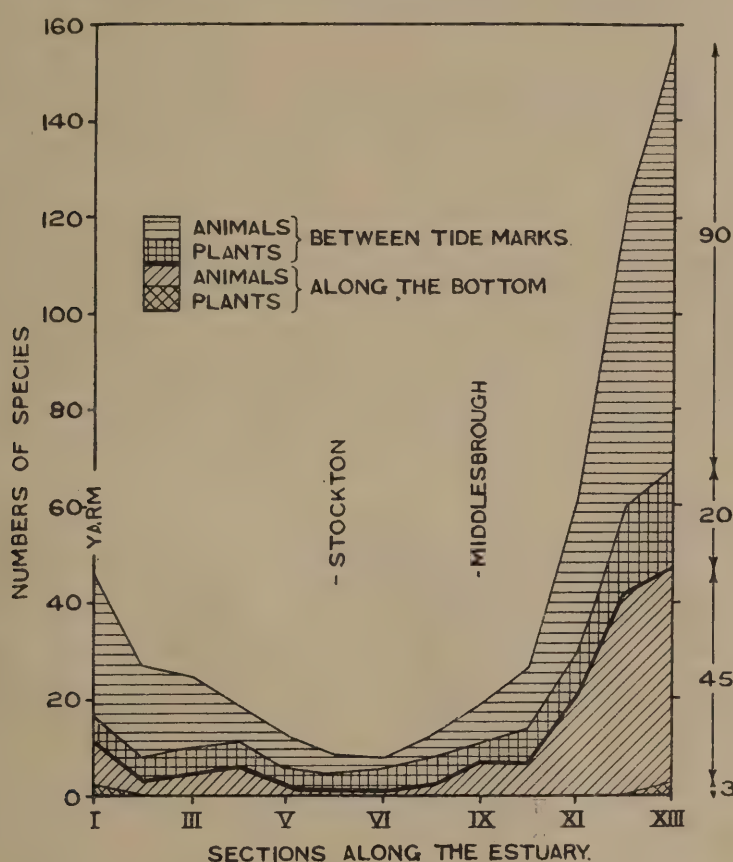


FIG. 23—Variation in Numbers of Species of Bottom and Tidal Animals and Plants along the Tees Estuary

The numbers of species in each of the groups in the estuarine fauna and flora are shown in Table 25.

Certain phyla, as indicated by the distribution of these species, showed a more general adaptation to the varying estuarine conditions than other phyla. Species of Annelida and Arthropoda formed most of the fresh water and a large part of the marine fauna. Among plants, which, except for two species of mosses, were all algae, the brown algae were the most numerous.

Of the fourteen phyla in Table 25 only five had both marine and fresh water species in the Tees. With the Arthropoda, Annelida and green algae the ranges of the marine, fresh water and brackish water species overlapped and some species of each group were to be found in all sections. The ranges of the fresh water and marine sponges and molluscs did not, however, overlap, and there was a large gap in the central reaches where no sponges or molluscs occurred. Johansen<sup>(23)</sup> noted that molluscs did not occur in North Europe in brackish water of low salinity. The most numerous group of plants—the brown algae—have no fresh water representatives and, although the marine species penetrated to a great distance from the sea, this group was absent from the fresh water Sections I to III.

TABLE 25—*Number of Species of Animals and Plants Found in the Tees Estuary*

Group.	Section.														
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	SXII	SXI
PORIFERA (Sponges)	1	—	—	—	—	—	—	—	—	—	1	3	2	—	—
COELENTERATA															
Hydroids	—	—	1	1	1	1	—	1	1	1	6	10	14	4	1
Anemones, etc.	—	—	—	—	—	—	—	—	—	—	1	2	5	1	—
PLATYHELMINTHES (Flatworms)	2	1	2	—	—	—	—	—	—	—	—	—	—	—	—
NEMERTINI	—	—	—	—	—	—	—	—	—	—	—	2	2	—	—
ANNELIDA (Worms)															
Polychaeta	—	—	—	1	1	1	1	2	5	5	13	20	22	7	5
Oligochaeta	2	2	2	2	2	2	—	2	2	2	2	1	1	—	—
Hirudinea (Leeches)	3	2	2	2	1	—	—	—	—	—	—	—	—	—	—
ARTHROPODA															
Crustacea, etc., (Crabs and Shrimps)	3	2	2	1	1	1	1	2	3	5	9	26	31	12	9
Insecta (Insecta larvae)	18	11	4	1	—	—	—	—	—	—	—	—	—	—	—
MOLLUSCA (Sea slugs, snails and bivalves)	2	2	3	1	1	—	—	—	—	2	7	17	20	8	2
BRYOZOA (Sea mats, etc.)	—	—	—	—	—	—	—	—	—	—	2	3	6	—	—
ECHINODERMATA (Sea urchins and star fishes)	—	—	—	—	—	—	—	—	—	—	2	2	5	2	—
TUNICATA (Sea squirts)	—	—	—	—	—	—	—	—	—	—	—	2	5	1	—
BRYOPHYTA (Mosses)	1	2	2	1	—	—	—	—	—	—	—	—	—	—	—
ALGAE															
Chlorophyceae (green)	3	2	3	3	3	4	3	4	2	4	2	6	5	2	3
Phaeophyceae (brown)	—	—	—	1	1	—	2	2	2	3	5	8	10	3	2
Rhodophyceae (red)	—	—	—	—	—	—	—	—	—	—	1	3	6	1	—
Total species	35	24	21	14	11	9	7	13	15	22	51	105	134	141	22

In considering the penetration of the Estuary by the flora and fauna, it was found that the range of species even of the same phylum differed greatly. Among those which penetrated the Estuary for a considerable distance three species of green algae were notable. *Enteromorpha compressa* and *E. intestinalis* were found from the sea to III, at the limit of salt water, whilst *Vaucheria piloboloides* extended into the fresh water reaches to I. The brown alga *Fucus vesiculosus* was found up to IV, and a worm *Nereis diversicolor* had a similar extended distribution to IV, where



the water at high tide had usually a salinity of about 10 gm. per 1,000 gm. but might at times be fresh. The range of fresh water species was considerably restricted when compared with the marine species, since none except *Cladophora* sp. penetrated below VI, and many species died away before the influence of salt water was apparent. The distribution of certain species of *Gammarus* in the Tees differed from their distribution in other estuaries. Two marine species, *G. locusta* and *G. marinus*, extended further into the Tamar estuary than into the Tay or Tees and further into the Tay than the Tees. *G. duebeni* has a peculiar distribution. In the Tees and Tamar it occupied Sections I to V or VI. In the Tay, however, Sections I to IV were occupied by *G. zaddachi* and the stretch occupied by *G. duebeni*, instead of being shortened, was pushed downstream to Sections V to X, overlapping the ranges of *G. locusta* and *G. marinus*.

A species of bug (*Aphelocheirus aestivalis*) was found at Yarm in I, but occurred nowhere else in the whole river.

The fauna and flora of Seaton Channel consisted mainly of species which were also found in the main channel, but had some peculiar features. Several surveys at high and low water indicated that the water in S XII and S XI was of a higher salinity than that of the main channel. Table 25 shows, however, that the fauna and flora died away more rapidly than in the main channel, and it seemed probable that the presence of mud both on the foreshore and the bottom produced a uniformity of habitat not suited to a wide variety of marine organisms. *Ascophyllum nodosum* was much more abundant in S XII than in the main channel, and it seemed probable that the training wall was too low in XII for the development of this plant. Although the cockle (*Cardium edule*), a clam (*Mya arenaria*), and a mud-burrowing crustacean (*Corophium volutator*) have been found in the main channels of other estuaries, *Cardium* was rare in the Tees main channel and the other two were absent. In the mud flats of S XII, however, all three species were abundant.

Apart from the normal seasonal changes which occur in the abundance of various organisms, such as the dying away of hydroids in the winter and the seasonal maxima of insect larvae, no seasonal changes were observed in the fauna and flora of the Estuary and only two changes were observed between different years. In 1931 the brackish water hydroid (*Cordylophora lacustris*) was found to have extended the lower limit of its range from Stockton (VI) to Middlesbrough, where it was found near low-water mark on wharves in VIII and IX. The bladder-wrack seaweed (*Fucus vesiculosus*) extended in 1929 and 1930 from the sea to VII. In 1931, however, small plants were discovered growing in V and IV, a distance of four miles above the previous limit of distribution.

Many marine species—mainly animals—are of special importance. The wood-boring gribble (*Limnoria lignorum*), for example, damages wooden piers, wharves and other harbour works. This species was found only in XIII, XII and XI, and the damage caused was limited to Redcar Jetty, 5th Buoy Lighthouse, occasional structures such as lights and beacons along the channel and, to some extent, the Teesport wharves. From the experiments of other workers<sup>(24)</sup> on the resistance of *Limnoria* to varying salinity conditions, it seems probable that its distribution in the Tees is not restricted by pollution, and that the limited amount of damage caused by it is due to the absence of extensive wooden structures within its range.

Evidence of the decline of the salmon and sea-trout fisheries in the Tees, probably caused by pollution, is given in Chapter I. Past records of the abundance of marine fish in the Estuary are not available, but it is recorded by fishermen that numbers of codling and flat fish were obtainable some years ago at least as high as X. XIII is now the only section worth fishing with lines and hooks. Shellfish, mainly mussels (*Mytilus edulis*), cockles (*Cardium edule*), and periwinkles (*Littorina littorea*), were at one time gathered extensively for sale as human food. Of recent years very few have been collected for this purpose and the collection of Tees shellfish for human consumption is now prohibited on account of sewage pollution. The quotations on pages 63 and 66 indicate that the number of sea-birds has fallen considerably, and the seals have almost disappeared. The main causes are probably the reclamation of land and the population of the banks.

#### ANIMALS FOUND ON L.N.E. RAILWAY DOCK GATE

Beaching of the gate of the L.N.E. Railway Dock in Section X afforded an opportunity of examining the animals growing on its outward, tidal face. All

the animals found were marine and the growth, which was not abundant, consisted mainly of Mussels (*Mytilus edulis*), Hydroids (chiefly *Laomedea gelatinosa*), and a large colony of the anemone, *Metridium senile*. Table 26 gives the highest sections in which the species were previously found.

TABLE 26—*Marine Animals found on the L.N.E. Railway Dock Gate (Section X) near Middlesbrough, March, 1933*

	Highest Section in which previously found.
SPONGE—	
<i>Halichondria panicea</i> ... ..	XI
HYDROIDS—	
<i>Laomedea gelatinosa</i> ... ..	X
<i>Opercularella lacerata</i> (Johnston) ... ..	—
ANEMONE—	
<i>Metridium senile</i> var. <i>dianthus</i> * ... ..	XII
WORMS—	
<i>Lagisca extenuata</i> * ... ..	XII
<i>Nereis pelagica</i> * ... ..	XII
<i>Pomatoceros triqueter</i> ... ..	XI
BARNACLES—	
<i>Balanus crenatus</i> ... ..	XI
<i>Balanus balanoides</i> ... ..	VIII
MOLLUSCS—	
<i>Mytilus edulis</i> ... ..	X
ASCIDIANS—	
<i>Botryllus schlosseri</i> * ... ..	XII
<i>Botrylloides leachi</i> * ... ..	XIII
<i>Ascidella aspersa</i> * ... ..	XIII

Six of the species had been found previously in Section X or in the adjacent Section XI. One species (*Opercularella lacerata*) was not recorded elsewhere in the Tees and six species (marked with an asterisk) were not found higher than two miles seaward of the Dock Gates. No attempt was made to include these records in the main faunistic list since (a) the collection of specimens from the Dock Gate represents a much more intensive investigation of the bottom fauna than was possible in the open channel by means of dredge and trawl; and (b) the conditions obtaining in the dock cut are not identical with those of the main channel where there is no protection from strong currents, where industrial effluents in fairly high concentration may occasionally be washed direct from the outfall pipes and where the salinity of the water is directly and probably more affected by floods from the upper river.

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## CHAPTER VIII

## COMPARISON OF THE BIOLOGY OF THE TEES ESTUARY WITH THAT OF SOME UNPOLLUTED ESTUARIES

It was found that whilst the fauna and flora at both ends of the Tees Estuary were abundant, there was a marked scarcity of species in the middle reaches. In this discussion, marine species are assumed to be present in all sections seaward of those in which they were found, and fresh water species in all sections between Yarm (Section I) and those in which they were found. The numbers of fresh water species in each section are expressed as percentages of the number at Yarm (Section I) and the marine species as percentages of the number at the mouth (Section XIII). The three brackish water species are expressed as percentages of the total number of fresh water species.

It is pointed out later in this report that the central reaches of the Estuary contained directly poisonous substances, and that in addition the water in these reaches was partially deoxygenated as the result of the decomposition of sewage and industrial effluents. Since both the sewage and industrial wastes are discharged at about the same position in the Estuary, the amount of deoxygenation of the water gives a rough index of the total amount of pollution.

From the data in Chapters III and IV the curve in Fig. 24 was drawn to show average concentrations of dissolved oxygen in different parts of the Estuary when the temperature of the water was between  $13^{\circ}$  and  $16^{\circ}$  C. The same diagram

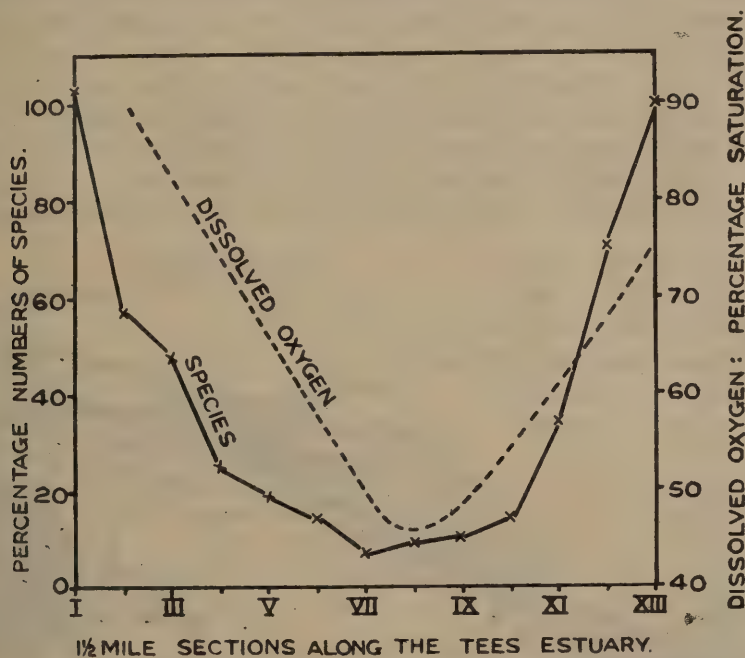


FIG. 24—Average Percentage Saturation of Dissolved Oxygen at  $13^{\circ}$  to  $16^{\circ}$  C. and Percentage Numbers of Species in the Tees Estuary

includes a curve showing the relative numbers of species in different parts of the Estuary. The smallest number of species occurred in the area of maximum pollution, and the possibility arises that this was due to pollution. It is well known, however, that marine animals and plants cannot, as a rule, live in fresh water, and that as the Estuary is ascended the decreasing salinity will cause the disappearance of the marine species. Similarly, the increasing salinity as the Estuary is descended will cause a gradual disappearance of fresh water species. Fig. 22 shows that this was the type of distribution which occurred in the Tees Estuary.

From a consideration of the Tees alone it could not be decided whether the scarcity of organisms in the middle stretch was due to adverse salinity conditions or to the effects of pollution. For comparison, the distribution of animals and plants in the unpolluted Firth of Tay was examined.

## THE FIRTH OF TAY

The source of the River Tay is on Ben Lui, 3,000 ft. above sea level<sup>(1)</sup>. In a distance of 11 miles it falls 2,500 ft. and enters Loch Dochart, and then, known as the River Dochart, it runs 11 miles into Loch Tay. The overflow from Loch Tay is called the River Tay, and although down to Perth it is still a fast river with current speeds up to three miles per hour, the fall is no longer as rapid as in the higher reaches. Tidal action is noticeable one mile above Perth and the river flows into the North Sea by way of a broad estuary 32 miles in length. The distance traversed from Ben Lui to the sea is 117 miles. Six miles below Perth the River Earn discharges into the Firth of Tay from the south. The River Earn is a river of about the same size as the Tees, whilst the Tay is much larger, having an average flow of the order of 150,000,000 cu. ft. per 12 hours compared with about 15,000,000 to 20,000,000 cu. ft. for the Tees.

In choosing the Firth of Tay for comparison with the Tees Estuary, the following features were considered :—

1. The Tay is a fast flowing river with soft water and is subject to rapid rises in level and to "brown" peat floods similar to those of the Tees. Hence the fresh water fauna and flora of the two rivers may be expected to contain species common to both.
2. Although the Tay is larger than the Tees, the Firth of Tay being larger than the Tees Estuary makes it probable that the salinity conditions in the two estuaries are similar. With rivers such as the Findhorn, Spey, Don, and Tweed, the water at low tide is fresh throughout most of the length of their small estuaries.
3. Both the Tees and Tay discharge their waters into the North Sea, so that the marine organisms near the mouths of the Estuaries are recruited from the same stock and should contain many species in common.

The Firth of Tay is a broad, comparatively shallow estuary with a sandy bottom. Below the confluence of the Earn and Tay the estuary, after widening to over 3 miles above Dundee, contracts to a width of about 1 mile at Tayport. In Fig. 25 the approximate positions of the banks exposed at low water are shown by the shaded areas, whilst the black areas indicate depths of over 3 fathoms.

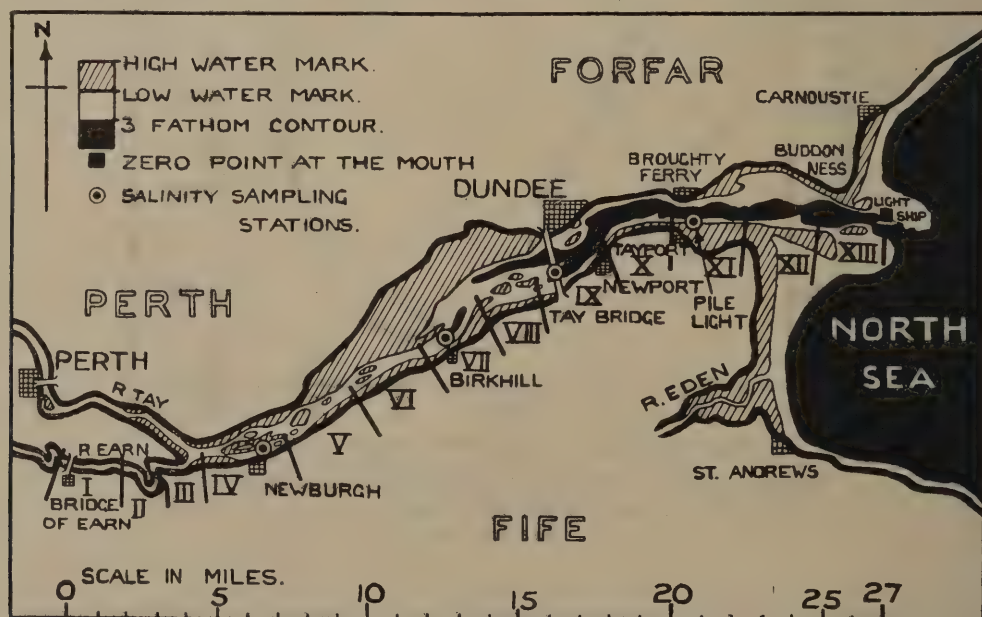


FIG. 25—Firth of Tay, Scotland

It will be seen that a very large proportion of the area of the estuary above Dundee, chiefly along the north shore, is exposed at low water, leaving a channel near the south bank. Banks with less than 3 fathoms of water over them at low water extend along both sides of the mouth of the estuary for several miles. The channel between them is comparatively deep, exceeding 10 fathoms in the centre near Tayport, and water of over 3 fathoms extends above the Tay Bridge for some distance. The bottom of the channel and the banks exposed at low water on the south shore consist almost entirely of sand. In places there are patches of mud, especially near the mouth of the Earn and at the points where various small



streams enter the estuary, but these patches are usually not more than a foot deep, and fishermen stated that they were, for the most part, only temporary deposits of material brought down by floods and liable to be removed by succeeding spates. The large bank on the north side consists of a wide belt of mud adjoining the shore; this mud merges gradually into sand as the centre of the estuary is approached. This bank was not examined.

From Newburgh to Tayport the Ochil Hills run close to the southern shore of the Firth, and the south bank in some places has low cliffs with numerous sections of rocky or stony shore. These provide firm holding ground for seaweeds and sessile animals and shelter for others, similar to that given by the slag training walls along the banks of the Tees.

Above the confluence of the Earn and Tay biological collections and water samples were taken in the Earn, in order to avoid the possible effects in the narrow reaches of the Tay of pollution from Perth. The Earn is tidal for over 10 miles before joining the Tay, and at Bridge of Earn, some 7½ miles from the Tay, the rise of tide amounts to several feet. Below the confluence of the two rivers collections and samples were taken along or within 50 yards of the south bank. The width of the estuary at Dundee (about 2 miles) makes it improbable that pollution from Dundee on the north bank would seriously affect the water or organisms near the south bank. Below Tayport the sand banks on the south side which run out some distance to sea are barely exposed at low water, so that collections had to be made on the north bank at Buddon Ness.

Salinity Conditions

The mean range of springs at Dundee is 14·8 ft., and the mean range of neaps is 8·8 ft. The corresponding values for the Tees (5th Buoy Lighthouse) are 14·7 ft. and 7·4 ft. High water at Newburgh occurs about ¾ hour after the time of high water at Dundee and at Bridge of Earn about 1¼ hours later than at Dundee. At Bridge of Earn the tide ebbs for about 10 hours and flows for about 2 hours.

During a preliminary survey of the Firth of Tay two series of samples, taken from a boat running steadily from one end to the other, showed that the salinity rose gradually as the mouth of the estuary was approached. In a more detailed survey during August and September, 1930, four stations, spaced at approximately

TABLE 27—Average Salinity at High and Low Water 50 Yards from the South Shore in the Estuary of the Tay

Position.  Miles from Abertay Lightship.	Average salinity at high water.			Average salinity at low water.		
	Surface.	1 Fathom.	Bottom.	Surface.	1 Fathom.	Bottom.
Newburgh 23 miles.	1·2 (5)	1·3 (5)	2·3 (5)	—	—	—
Birkhill Pier 16½ miles.	13·0 (4)	13·4 (4)	15·3 (4)	0·0 (5)	0·0 (5)	0·0 (5)
Tay Bridge 12 miles.	18·4 (9)	19·3 (9)	22·0 (9)	2·5 (10)	3·0 (10)	3·5 (10)
Pile Light 7 miles.	25·8 (4)	27·5 (4)	28·7 (4)	13·6 (6)	13·8 (6)	18·4 (6)

equal distances throughout the estuary, were chosen (Fig. 25), and samples were taken at times of high and low water. This method was adopted in order to determine the extreme conditions of salinity occurring at these points, and also because several determinations at the same place and at the same state of tide, but under different conditions of fresh water flow, etc., are necessary before a representative value for the average salinity can be obtained. The average salinities at the four sampling stations are given in Table 27.

A comparison of the average salinities in Table 27 with those found in the Tees Estuary is made in Fig. 26. The vertical salinity gradient, which is so marked a feature of the Tees Estuary, is very small in the Firth of Tay.

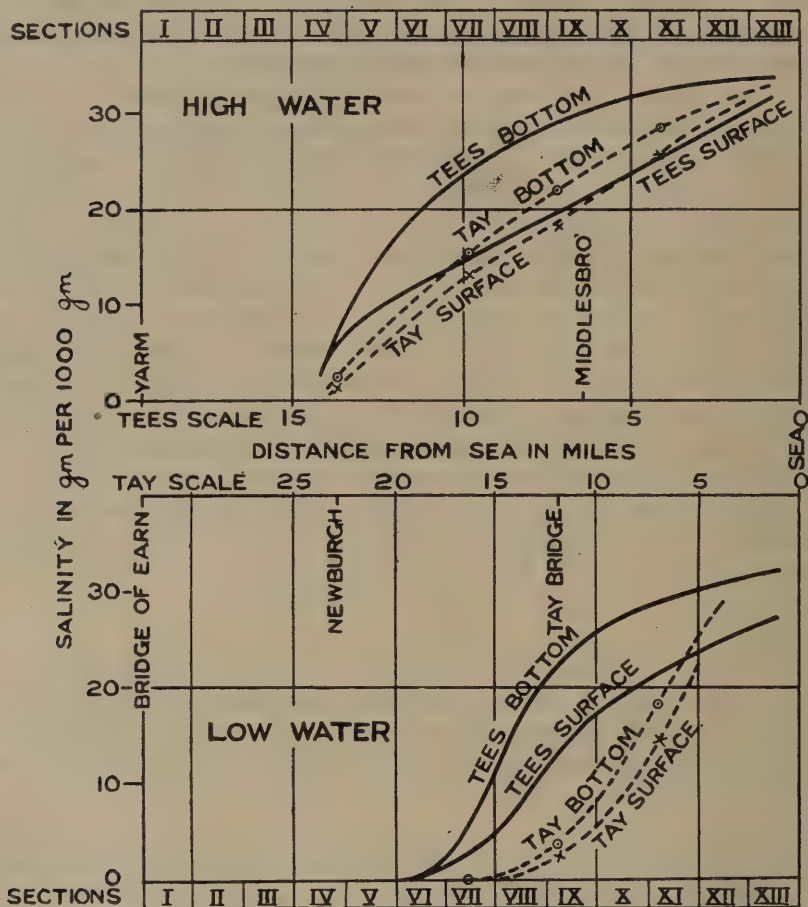


FIG. 26—Average Salinity at High and Low Water in the Estuaries of the Tees and the Tay

From the preliminary results obtained in June, 1930, it appeared that salt water penetrated further from the sea in the Tay than in the Tees. On the average the increase of salinity in the Tay in a distance of 5 miles seaward was about equal to that in the Tees in a distance of 3 miles. Accordingly, as records of the distribution of species in the Tees had been worked out for each section of  $1\frac{1}{2}$  miles, collections were made in the Firth of Tay in sections each  $2\frac{1}{2}$  miles long, giving the same number of sections (13) between Bridge of Earn and the Abertay Lightship as in the Tees between Yarm and No. 2 Buoy. The average salinities given in Table 27 for the Firth of Tay are not quite so high as those for corresponding sections in the Tees Estuary. This is due to the fact that the Firth of Tay was divided into sections on the basis of the salinity data collected during a dry weather period in June, 1930. The data were, in consequence of the dry weather, higher than the results obtained in the more detailed survey in August and September, 1930.

The number of salinity determinations on which the curves for the Firth of Tay are based is much smaller than is the case for the Tees Estuary, and the former are therefore not so reliable. The River Tay was fairly high during the period of sampling and, as was shown for the Tees Estuary, this may have produced a downstream movement of the saline waters. Conditions of spate are also favourable for the development of a vertical salinity gradient since the fresh water tends to run away on the surface. It is probable, therefore, that the vertical salinity gradient is smaller under average conditions of fresh water flow than is shown by Fig. 26, and is almost absent under dry weather conditions. Indeed, during short surveys of the Tay in June, 1930, and later in June, 1932, when the river was low, the greatest difference in salinity between surface and bottom samples at any station amounted to only 1 gm. and 3 gm. per 1,000 gm., whilst the average difference at the Tay Bridge for the wet period, August and September,



1930, was 3.6 gm. per 1,000 gm. In Fig. 27 the maximum and minimum salinities observed in the Tees and Tay are compared. The extreme conditions in corresponding sections are similar.

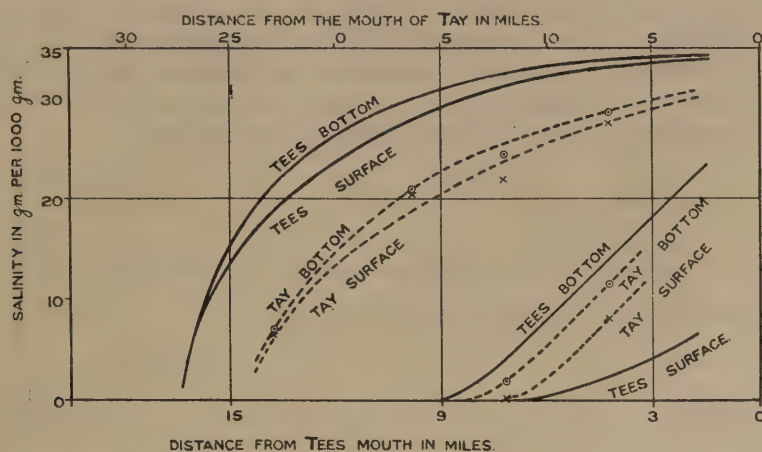


FIG. 27—Maximum and Minimum Observed Salinities in the Estuaries of the Tees and the Tay

### *Dissolved Oxygen and pH values*

All samples of water collected in the estuary of the Tay contained high concentrations of dissolved oxygen, the average being nearly 90 per cent. and the range from 85 to 104 per cent. of the saturation values at the temperatures of the samples 13° to 17° C. The pH values found ranged from 6.6 to 7.2 in fresh water and rose to a maximum of 8.2 in water of salinity 30 gm. per 1,000 gm.

### *Fauna and Flora*

Biological collections in the Firth of Tay were made at one or two stations in each of the thirteen sections into which the estuary was divided<sup>(2)</sup>. The distribution of each species obtained is given in the fauna lists in Chapter VII. As in the Tees, marine animals were assumed to be present in all sections seaward of those in which they were found, and fresh water animals up to Section I from the sections in which they were found. In the Tees the amount of collecting done was much greater than in the Tay, with the result that the numbers actually found approach much more nearly to those assumed than do the numbers found in the Tay. The diagram showing the relative importance of marine, brackish water and fresh water organisms in different sections of the Tay (Fig. 28) was prepared from the assumed numbers of species. The relative abundance of the different groups of organisms is very similar to that found in the Tees (Fig. 22).

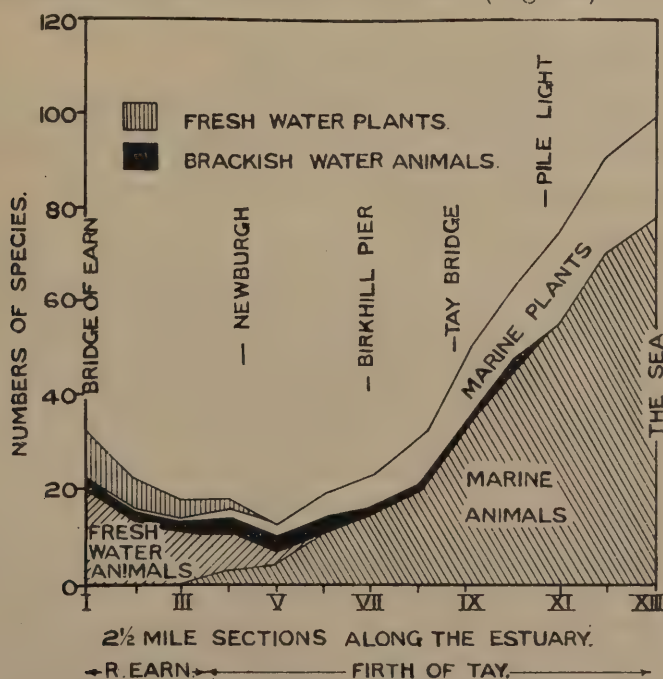


FIG. 28—Composition of the Fauna and Flora along the Firth of Tay

In Fig. 29 a species distribution curve (similar to Fig. 24 for the Tees) is shown with a curve for average concentrations of dissolved oxygen along the Firth of Tay. From a comparison of Figs. 24 and 29 it appears that the general distribution of species in the middle stretch of the Tees Estuary is not affected primarily by pollution. The same scarcity of organisms in the middle stretch occurs in the Tay where the salinity conditions are similar but where there is little or no pollution and the dissolved oxygen concentration is high. It seems possible that the main controlling factor in each case is the salinity.

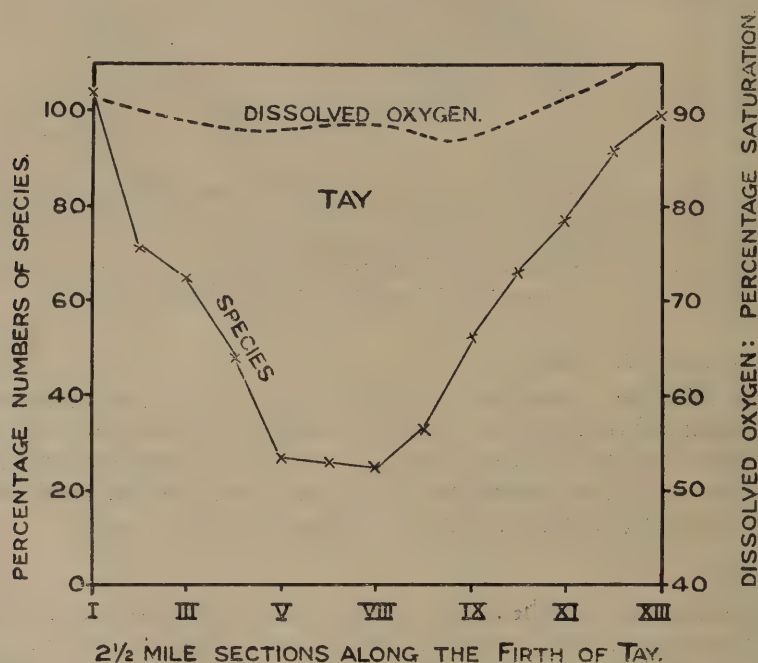


FIG. 29—Average Percentage Saturation of Dissolved Oxygen at 13° to 16° C. and Percentage Numbers of Species in the Firth of Tay

In a tidal estuary, especially one like the Tees where there is a marked vertical salinity gradient, organisms living between tide marks are subject to conditions different from those along the bottom. In order to define the salinity conditions as they affect living organisms at a given position and level in an estuary, it is desirable to assess :—

1. The mean salinity over a long period.
2. The average variation in salinity over a long period caused by tidal movements and by the inflow of fresh water from the upper river.
3. The maximum and minimum salinities experienced.

An estimate, for the Tees, of the variation in salinity along the bottom due to tidal movement and varying fresh water flow was obtained from the differences between the salinities at certain positions at low water under normal winter conditions and at high water under normal summer conditions. These two extreme values are the lower and upper limits of salinity to which an organism will normally be exposed. The variation in the inter-tidal area, which is an important habitat with a characteristic fauna and flora, is more difficult to assess. At an ordinary low water only the organisms living in the lowest part of the area are exposed directly to the estuary water, and at high water an animal or plant living on the inter-tidal foreshore may be submerged only a few inches or more than 2 fathoms. The salinity variation to which an organism is subjected depends, therefore, on the position in the inter-tidal area at which the species normally lives. A mean value has been taken as the difference between the salinity at the surface at low water under normal winter conditions and at a depth of one fathom at high water under normal summer conditions. Organisms living near high water mark suffer a smaller, and those living near low water mark a greater



variation than this mean value. The variations thus obtained for the inter-tidal area and at the bottom are shown in Fig. 30.

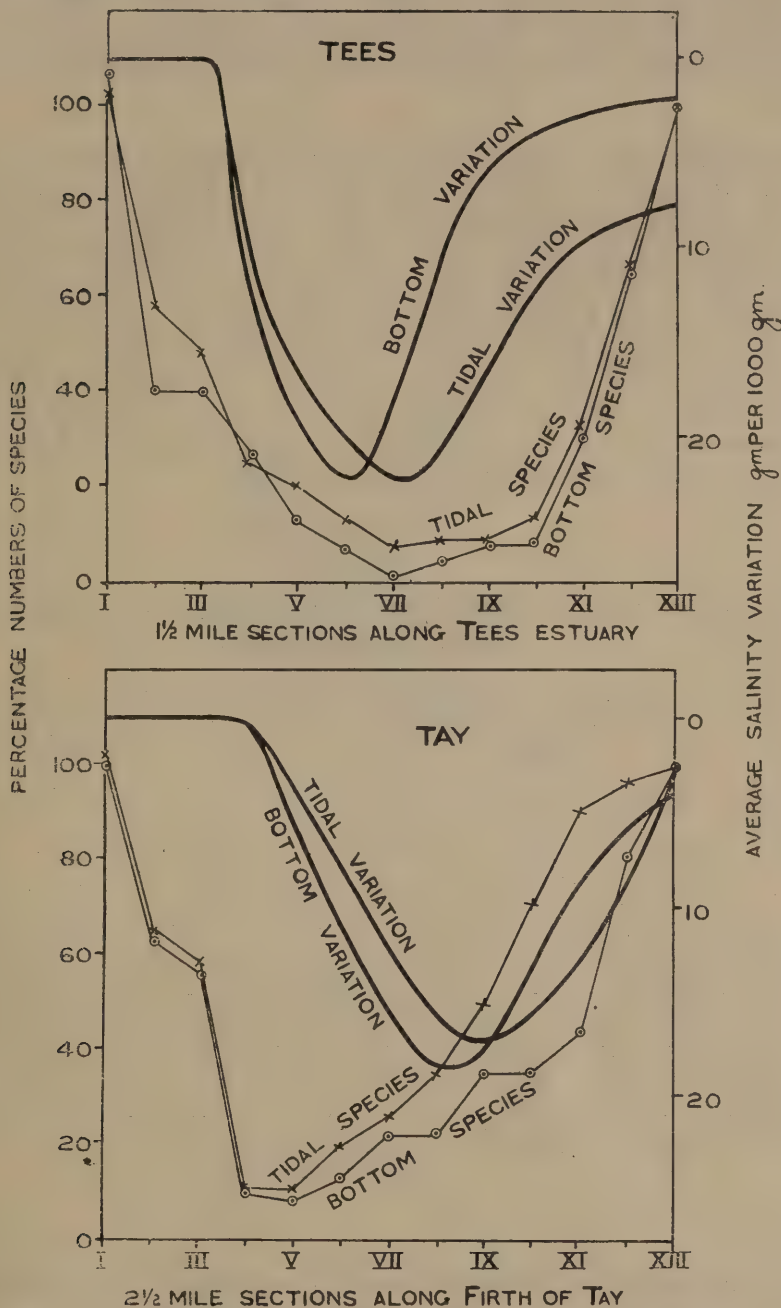


FIG. 30—Average Salinity Variation and Percentage Numbers of Species along the Tidal and Bottom Areas in the Tees Estuary and the Firth of Tay

The area of maximum variation is further up-stream at the bottom than between tide marks. The maximum variation at the bottom occurs at Stockton, where the water at low water is never more than slightly brackish but the bottom salinity at high water is considerable. The variation in salinity seaward of Stockton is considerably greater in the inter-tidal area than at the bottom, since the disturbing effects of floods from the upper river are mainly felt in the surface layers.

The salinity variations for inter-tidal and for bottom areas in the Firth of Tay were calculated from the data given in Table 27, in the same way as for the Tees Estuary. Animals and plants have been classified as bottom and tidal species and the percentages, calculated as before, are plotted in Fig. 30, which also includes curves showing variations in salinity.

In the Tees Estuary the minimum number of species occurs in the region in which the salinity variation is greatest, and the curve of the number of species follows fairly closely the curve of salinity variation.

In the Firth of Tay, however, although increasing salinity variation may account for the fall in the numbers of marine species from the sea to Section IX, it leaves unexplained the continued fall in numbers from VIII to V where the salinity variation decreases. Moreover, in both estuaries there is a rise in the numbers of fresh water species from IV to I, where, although tidal, the water is always fresh.

Tidal conditions were investigated simultaneously in Sections I, II and III of the Tees, by the measurement of current speeds at the approximate centre of each section over a full tidal period of 12 hours. The periods of slack water are shown in Table 28. The period of slack water during which sedimentation might occur was not markedly different in the three sections, and the fall in the numbers of fresh water species from I to III does not appear to be due to this cause. The maximum current speeds in II and III were definitely higher than in I, whilst the average current speed (obtained by averaging the speeds every quarter hour for 12 hours) shows an increase from I (1.3 ft. per sec.) to II and III (1.6 and 1.8 ft. per sec. respectively). It seems possible that the increasing strength of current may in some way affect the fauna of these sections.

TABLE 28—*Duration of Slack Water in Sections I to III in the Estuary of the Tees (11th September, 1931)*

Section	Period with current speeds less than 1 ft. per sec.* Hours			Period with current speeds less than 0.6 ft. per sec.* Hours		
	High water	Low water	Total	High water	Low water	Total
I ..	1.1	0.8	1.9	0.4	0.4	0.8
II ..	0.9	1.2	2.1	0.4	0.9	1.3
III ..	0.8	0.4	1.2	0.2	0.2	0.4

\* Maximum current speeds :—Sections II and III, 2.5 ft. per sec.  
Section I, 1.9 ft. per sec.

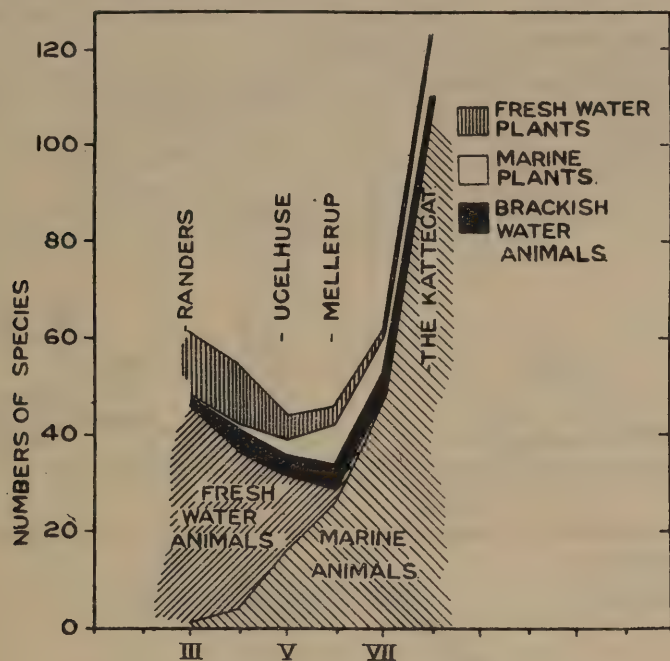
It thus appears that the distribution of organisms in an estuary may be affected by several factors. The disappearance of fresh water organisms began some distance above the salt water limit and cannot therefore be attributed to the effects of salinity. Fresh water organisms are, in general, not adapted to withstand inter-tidal conditions. Ascending the Tees Estuary from the seaward end there was a regular progressive reduction in the numbers of marine species, which was probably due to adverse salinity conditions. Although the organisms in the Tees and in the Tay were in general similarly distributed, many marine animals penetrated relatively further from the mouth in the Tay. These small differences may be related to the nature of the bottom and foreshore deposits. In the Tay the areas examined consisted of clean or fairly clean sand, while in the middle reaches of the Tees the bottom and parts of the foreshore consisted of black mud.

RANDERS FJORD

In Randers Fjord<sup>(3)</sup>, an estuary opening into the Kattegat on the east coast of Denmark, the rise and fall of the tide are very small and the variation of salinity in the middle of the Fjord is only 3 or 4 gm. per 1,000 gm. The salinity of the Kattegat itself is considerably lower than that of the North Sea, so that the conditions in the Fjord (Fig. 31) are entirely different from those of the Tees and the Tay, but, as in these estuaries, the variety of organisms in the middle reaches of the



Fjord is less than at the ends. It appears, however, that some marine animals are capable of penetrating relatively further into the Fjord, where the salinity is fairly constant, than into the British estuaries, where they are subject to large variations in salinity. One of the features of the Fjord is the variety of fresh water animals, mainly bivalve molluscs, occurring at about the limit of salt water penetration.



3-8 MILE SECTIONS ALONG THE FJORD.

FIG. 31—Composition of the Fauna of Randers Fjord

#### THE TAMAR ESTUARY

From data given by Percival<sup>(4)</sup> it has been possible to compare the fauna of the relatively unpolluted though muddy estuary of the Tamar with that of the Tees. The Tamar Estuary discharges, together with the Lynher and Tavy, into Plymouth Sound. The Estuary is winding and includes extensive mud flats. In the lower part, the Devon bank is lined by the Naval Dockyards. Salinity observations indicate that the salinity gradient would be comparable with that of the Tees Estuary if the Tamar Estuary were divided into compartments  $1\frac{1}{2}$  miles in length.

#### DISTRIBUTION OF FAUNA AND FLORA

The relative penetration of marine animals into Randers Fjord, the Firth of Tay, and the estuaries of the Tamar and Tees is shown in Fig. 32. The marine

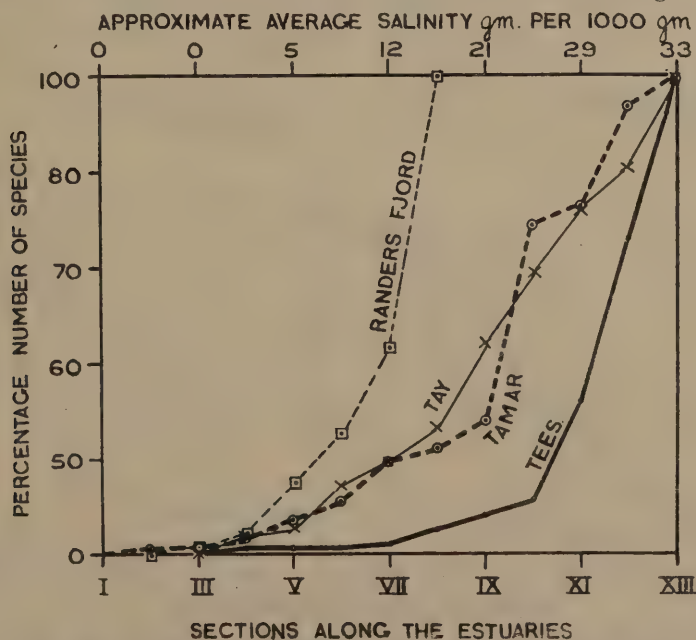


FIG. 32—Distribution of Marine Animals in Randers Fjord, the Firth of Tay and the Estuaries of the Tamar and the Tees

fauna of the Tees is less varied than that of the Tay and Tamar except at the mouth. In Fig. 33 is shown the distribution of all the species (plants and animals—fresh water, marine and brackish water) found in any two of these British estuaries and also those common to all three. The curves show that, of these common marine species, the numbers which survive in the central part of the Tees Estuary, especially in VII to IX, are fewer than those in the central part of either the Tay or the Tamar. The curves for the last two estuaries, one sandy and the other muddy, are in close agreement.

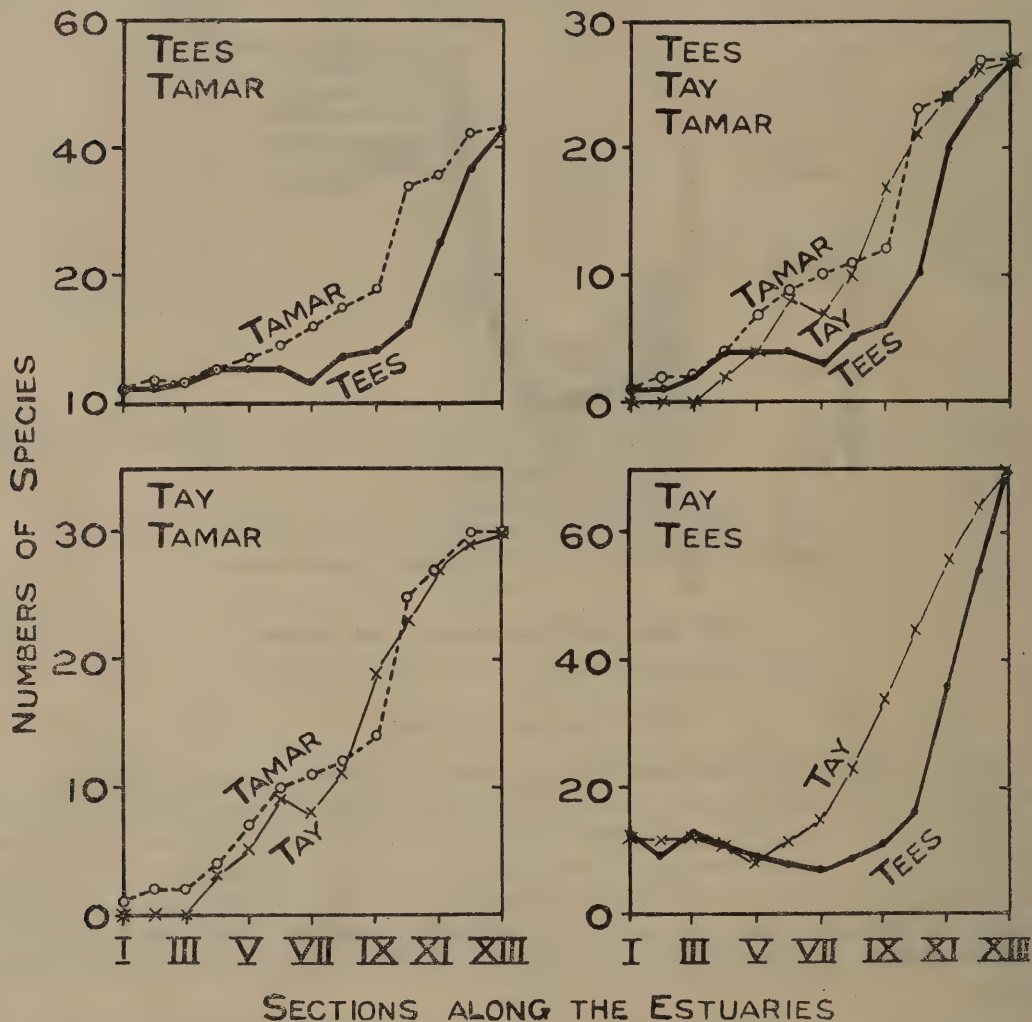


FIG. 33—Distribution of Species Common to the Estuaries of the Tees, Tay and Tamar

The marine animals common to the three estuaries were divided into "suspension feeders" and "non-suspension feeders" in an attempt to determine whether suspended matter affected the two groups differently. Fig. 34 shows

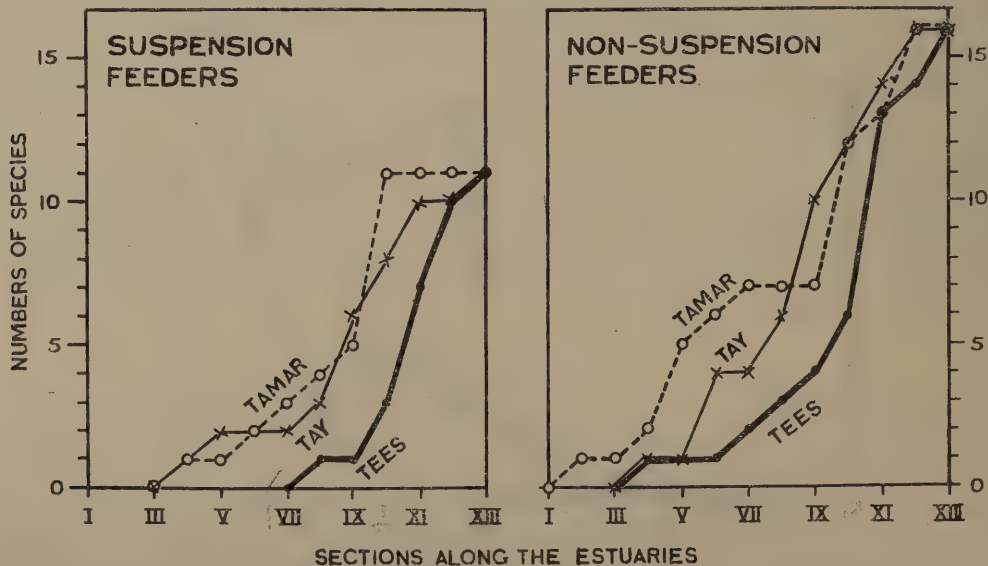


FIG. 34—Distribution of the 27 Species Common to the Estuaries of the Tees, Tay, and Tamar



the results of this division, and it will be seen that there is no marked difference between the groups and that the number of species in the Tees Estuary is less than in the Tay and Tamar in both groups in VI to XI.

The marine animals in each estuary were then divided into three groups: sand-living species, mud-living species and species associated with rocks or weeds. In the first group were included such forms as *Arenicola marina* which live in muddy sand, in order that the mud-living species should comprise only those species which live in soft mud. Forms such as mysids and shrimps were omitted. The extent to which each group of animals penetrates into the three estuaries is shown in Fig. 35. The fewest species of rock- and sand-dwelling forms are found in the Tees Estuary, but the mud-dwelling species in the Tees penetrate as far as those of the Tay and Tamar. The mud-living forms in the Tees comprise only 8 per cent. of the marine species, whilst the sand- and rock-living species together comprise 88 per cent. The lack of penetration by these two types of species is

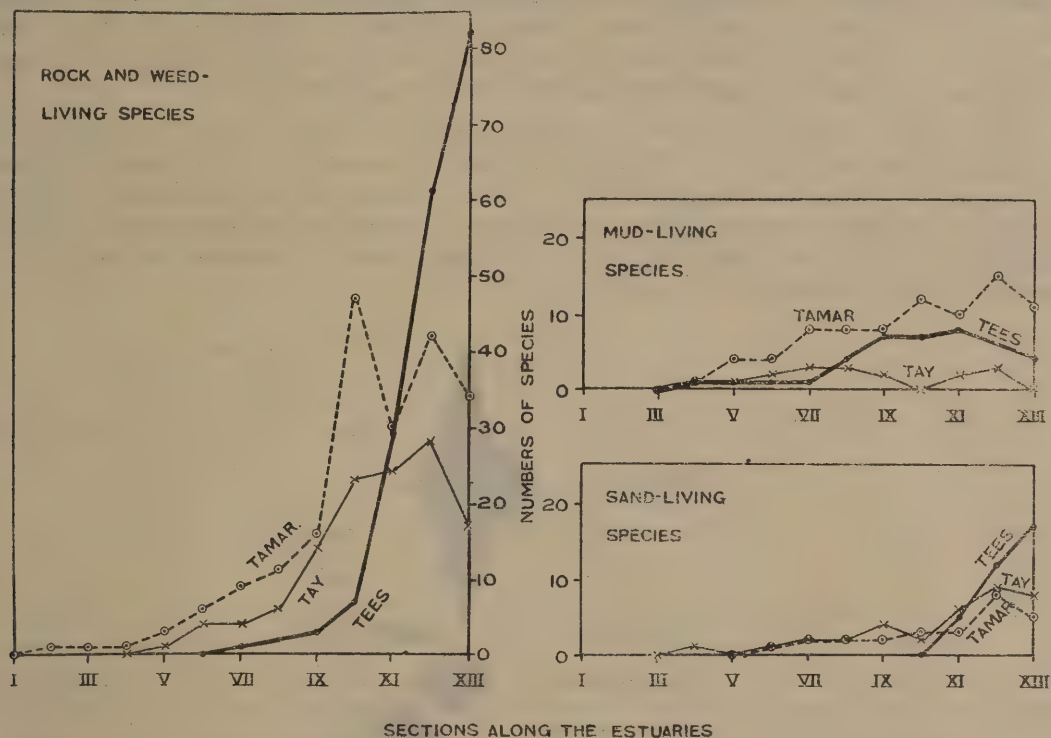


FIG. 35—Distribution of the Marine Fauna of the Estuaries of the Tees, Tay and Tamar

the cause of the scarcity of species in the Tees in VII to X. Penetration by sand-living species is prevented by the absence of any sub-stratum other than black mud or rock above X. In XI many weeds have already died away, and above this section the few weeds present are scattered and frequently carry mud on the fronds. The rocks also are covered by a thin layer of mud, and it seems probable that this habitat is unsuited to many types of rock- and weed-dwellers, since the majority are usually found in clean localities. In the Tay the mud occurs almost entirely on the north bank, while the south bank consists of clean rock and sand, and here sand- and rock-living forms are able to penetrate to a greater relative distance upstream than they are in the Tees. It is possible that the difference in distribution of mud and sand in the two estuaries is due, at least in part, to their different shape. A distribution of mud and sand similar to that found in the Tay has been observed in other estuaries where the mouth of the estuary is comparatively narrow and where there is a broad basin above.

In the Tamar Estuary, the organisms living in sand or muddy sand penetrate as far as the more varied sand-living organisms of the Tay.

It is possible that the distribution of certain species in the Tees may be affected by the discharge of direct poisons. Experiments on the susceptibility of a few species are described in Chapter XV.

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## CHAPTER IX

## QUANTITATIVE DISTRIBUTION OF CERTAIN SPECIES OF THE FAUNA AND FLORA AND THE EFFECT OF HABITAT ON DISTRIBUTION

In addition to the determination of the variety of species present in the Tees Estuary, some estimates were made of the density of population of the commoner animals.

One of the methods used was that employed by Stephen<sup>(1)</sup> in which the material from a given area is sieved and the animals are counted. The method is only applicable to areas of sand or mud. The material within an area of 0.25 sq. metre was dug out to a depth of about 30 cm. and washed with water through a sieve of perforated zinc with holes 2 mm. in diameter. With sand the method was satisfactory, but stiff mud would not pass through the sieve and it was necessary to break up the mud and pick out the worms contained in it.

The relative density of some common species in each  $1\frac{1}{2}$  mile section of the estuary is shown in Fig. 36. Besides the species shown in the Figure, 14 others were found in the areas sampled, but as these were either wandering forms or occurred only rarely they have been omitted. A small oligochaete worm, *Tubifex benedeni*, has also been omitted, as the 2 mm. sieve is unsatisfactory for the quantitative estimation of this species.

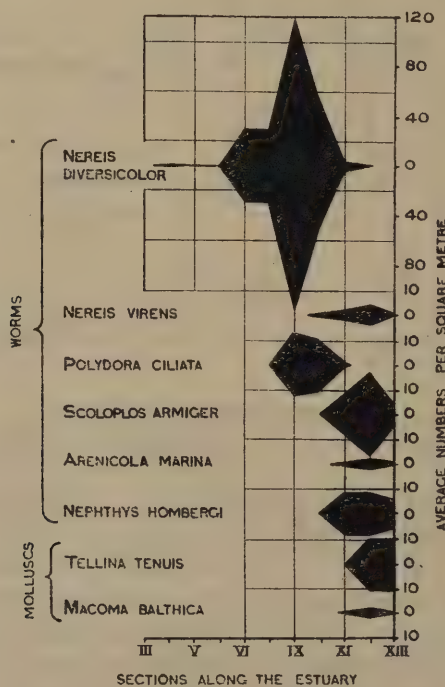


FIG. 36—Quantitative Distribution of Certain Burrowing Animals in the Tees Estuary

Of the eight species given in Fig. 36, only two extended for more than six miles from the mouth of the river. Of the remaining six species, five were forms which live in sand and therefore do not find a suitable habitat in the muddy reaches above Cargo Fleet. It is doubtful whether much significance can be attached to the results owing to the fact that in the upper part of the Estuary, above Section IX, the areas of mud exposed between tide marks are limited in extent and occur at different tide levels in different sections. For example, the abundance of *Nereis diversicolor* in VIII, IX and X (Fig. 36) is attributable in part to the fact that there are wide areas of suitable mud at the tide level at which *Nereis* is most abundant. The distribution of *Nereis* in the mud opposite Dock Point (X) illustrates the effect of tide level. At low water mark none was found; at about half-tide level there were 140 and at an intermediate position only 4 individuals per sq. metre. The scarcity of this species in V and VI may be due to the lack of mud banks at a suitable level.



*Polydora ciliata*, which builds tubes of mud, was most abundant in the muddy reaches of the Tees Estuary about IX. In XIII the sand was fairly clean and only *Tellina tenuis*, a mollusc which prefers clean sand, was found in abundance. The remaining species, living usually in rather muddy sand, were most abundant in XI and XII, where this type of beach is common. Above XI these species did not occur as the only tidal flats are of mud.

The results of some comparative determinations of the density of the fauna in clean sand in the Tay and Tees are given in Table 29, which shows that the productivity of the Estuary of the Tees at the mouth is of the same order as that of the Tay.

TABLE 29—Number of Animals per Square Metre at Two Localities in the Firth of Tay, and a Comparison with the Estuary of the Tees

Estuary.					Tay.		Tees.
Section.					XII.	XIII.	XIII.
Type of beach examined.					Shells and sand.	Clean sand.	Clean sand.
Species found	<i>Haustorius arenarius</i>	...	...	...	—	7	1
	<i>Crangon vulgaris</i>	...	...	...	2	—	—
	<i>Nephtys hombergi</i>	...	...	...	14	16	11
	<i>Nerine cirratulus</i>	...	...	...	40	1	4
	<i>Nereis pelagica</i>	...	...	...	—	2	—
	<i>Tellina tenuis</i>	...	...	...	—	2	21
	<i>Arenicola marina</i>	...	...	...	—	—	2
	<i>Nereis virens</i>	...	...	...	—	—	1
	<i>Scoloplos armiger</i>	...	...	...	—	—	8
	<i>Lanice conchilega</i>	...	...	...	—	—	2

The relative abundance of the periwinkle *Littorina littorea* throughout its range of about 6 miles in the Tees is shown in Fig. 37. At each locality sampled the numbers found in six separate ¼-metre squares were counted. All the stations were on the training wall, except that at the mouth, which was on the South Gare Breakwater. The results may have been influenced by the fact that the training wall becomes lower towards the sea and at the last two stations where collections were made it was almost below the level occupied by this species.

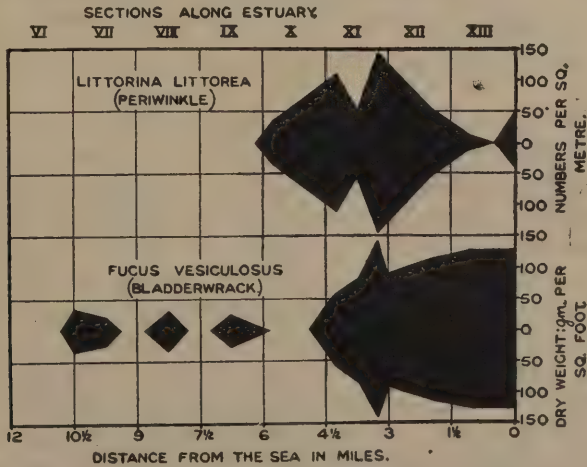
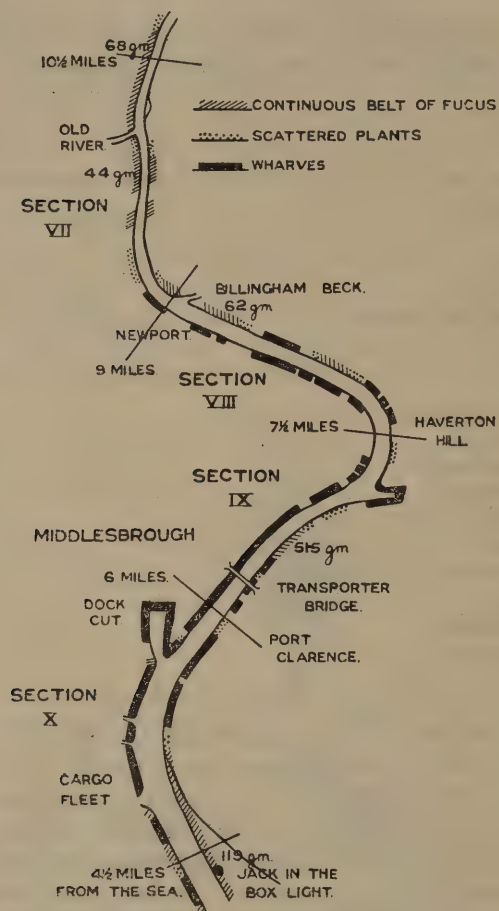


FIG. 37—Quantitative Distribution of Two Surface Living Species in the Tees Estuary

The common bladderwrack, *Fucus vesiculosus*, formed a belt of vegetation on the shore at about half-tide level from the sea to Cargo Fleet, and occurred at intervals higher up the Estuary to Stockton. In 1931 this limit was extended to two miles above Stockton (about 14 miles from the sea) when small and scattered plants were discovered in Sections IV and V. The distribution of this sea-weed

between Cargo Fleet and Stockton is shown in Fig. 38. The growth was mainly confined to the sloping banks faced with slag and rarely occurred on piles. Apart from the wharves, the positions of which are indicated on the map, both banks appear almost entirely suited to its requirements but it was unaccountably patchy in its distribution. From Dock Point to Newport (about  $3\frac{1}{2}$  miles) it was entirely absent from the Yorkshire side; this may perhaps be due to the amount of tarry matter usually present as a deposit on this bank or to greater toxicity of the water along the south bank (Chapter XIV). Above Newport the plant reappeared on the Yorkshire bank but soon disappeared from the Durham shore, although in this region both sides of the river appear to be similar and consist of slag-faced slopes.



Numbers show the dry weight of *Fucus vesiculosus* in gm. per square foot at the position of greatest density.

FIG. 38—Distribution of *Fucus vesiculosus* in the Tees Estuary

A quantitative determination of the abundance of *Fucus vesiculosus* at various points was made by collecting all the plants growing in an area of a square foot and determining their weight after drying. In each case the square foot was measured in the position where the plants appeared to be most abundant, and the results, irrespective of whether the plants were collected on the north or south shore, are plotted in Fig. 37. From the sea to Cargo Fleet there was a steady decline in density and shortly above this point the plant disappeared. Beyond Cargo Fleet it only occurred in patches, and wherever these were dense the order of density was about the same (44–68 gm. per square foot). The densest patch measured anywhere above Cargo Fleet was above the Old River in Section VII, and the species disappeared only a few hundred yards above this point. The abundance of *Fucus vesiculosus* below Cargo Fleet was probably influenced by the varying height of the training wall. Towards the lower end the wall was mainly covered with *Fucus serratus* and *F. vesiculosus* grew only along the top, mixed with *F. serratus*.

Dredging in the central reaches in the bottom mud showed that in certain places there were no worms present and that the mud had, occasionally, a tarry appearance. It seemed possible, therefore, that the tar was a governing factor in the distribution of the worms. Samples of mud were taken at 22 positions between Stockton and Jack-in-the-Box Light (VI to XI) using an apparatus similar to that described by Moore and Neill<sup>(2)</sup>; above and below this belt the bottom



is too hard to be sampled. Six samples were taken at each position ; one was used for chemical examination and five (representing an area of 1/115 sq. metre) were washed through cloth and the animals were counted. The only organisms found were five species of worms, and, of these, two species of polychaetes occurred only in two or three samples. The remaining species were oligochaetes of the genus Tubifex. Two were marine, *Tubifex benedeni* and *T. costatus*, and one was a fresh water species, *T. tubifex* (probably mixed with *Limnodrilus* sp.). The highest density of these oligochaetes recorded was, very approximately, 23,000 per sq. metre.

The concentration of substances extracted with benzol has been taken as a measure of the amount of tarry matter in the mud (Chapter VI).

There appears to be no correlation between the concentration of benzol extracts and the number of worms present. Although the small area sampled gives only an approximate idea of the numbers of worms present, Table 30 shows that the two marine oligochaetes can live in mud containing up to 0.64 per cent. by weight of substances soluble in benzol and are absent from certain other muds with concentrations of only 0.16 per cent.

TABLE 30—Fauna and Chemical Characteristics of Bottom Deposits in the Tees Estuary

Distance from sea. Miles.	Extracted material as percentage of dry weight.			Loss on ignition. Per cent. of dry weight.	Number of worms per $\frac{1}{115}$ sq. metre.	
	With petroleum ether.	With benzol.	Total.		<i>Tubifex tubifex</i> and <i>Limnodrilus</i> sp.	
11.3	0.52	0.14	0.66	16.8	47	
11.3	0.38	0.20	0.58	15.8	103	
10.6	0.36	0.48	0.84	19.9	94	
9.9	0.36	0.34	0.70	12.6	0	
9.0	0.58	0.44	1.02	17.6	0	
					<i>Tubifex costatus.</i> <i>benedeni.</i>	
8.6	0.06	0.04	0.10	13.4	10	87
4.7	0.28	0.10	0.38	20.5	169	1
6.8	0.30	0.12	0.42	15.0	64	0
7.3	0.48	0.16	0.64	16.5	0	0
4.2	0.22	0.20	0.42	19.3	141	13
6.8	0.55	0.20	0.75	14.5	183	18
5.7	0.42	0.34	0.76	19.4	3	0
7.8	0.66	0.34	1.00	26.6	0	0
7.4	0.40	0.36	0.76	16.3	0	0
6.1	0.46	0.36	0.82	19.2	237	2
5.2	0.44	0.38	0.82	20.2	0	0
5.0	0.65	0.40	1.05	21.6	62	0
8.5	0.42	0.44	0.86	18.4	0	0
8.2	0.54	0.50	1.04	16.6	0	0
8.2	0.46	0.58	1.04	18.4	0	0
6.4	0.85	0.64	1.49	18.6	70	0

THE SALINITY OF WATER RETAINED IN MUD

It has been shown (Chapter VI) that the water retained in the muddy foreshore is of a higher salinity than that which flows over it on the ebb tide. Fig. 39,

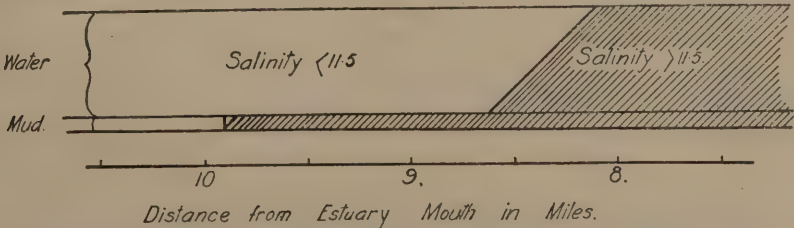


FIG. 39—Diagram illustrating the Distribution of Salinity at Low Water in the Water and Muddy Foreshore of the Estuary

based on actual observations, illustrates the conditions at Newport. It seems probable, therefore, that non-burrowing animals living in an estuary are subjected to greater variations and to lower minimum values of salinity than are burrowing forms at the same distance from the sea. It was observed that, both in the clean, sandy estuary of the Tay, and in the polluted, muddy estuary of the Tees, burrowing marine animals were, on the whole, relatively more abundant in the central part of the estuary than non-burrowers. In Fig. 40 the number of species of burrowing animals found in each of four sections of the Tees Estuary, expressed as a percentage

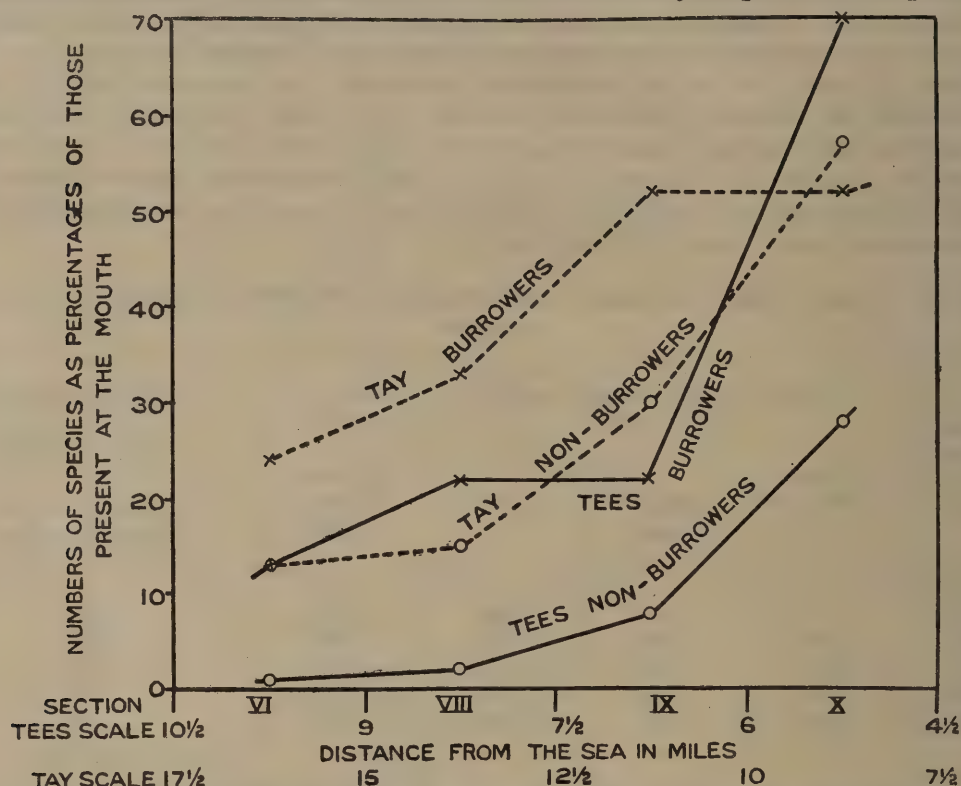


FIG. 40—Penetration of Burrowing and Non-Burrowing Animals in the Estuaries of the Tees and the Tay

of the total number of burrowing forms present at the estuary mouth, is compared with the corresponding percentage for non-burrowing animals. Similar figures are given for the Firth of Tay. The more stable salinity conditions obtaining in sand or mud appear to increase the range of burrowing marine animals when compared with non-burrowing forms.

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## CHAPTER X

## THE PLANKTON

The floating life or plankton of the sea consists mainly of small organisms which drift with the currents; it comprises a wide variety of both animals and plants. Since these organisms are always exposed to the effect of substances dissolved in the water, it was thought that the plankton of a polluted estuary might provide an index of the amount of pollution. During the Tees investigation surveys of plankton, covering a period of two years, were made throughout the Estuary.

The method first adopted was to run through the Estuary by motor launch at about the time of high water, starting in the upper reaches and descending to the sea. Samples were taken at positions 4,000 ft. apart. A conical tow-net, 100 meshes to the inch,  $3\frac{1}{2}$  ft. in length and with a circular mouth  $1\frac{1}{2}$  ft. in diameter, was used. The net was towed through the surface waters for three minutes, including  $\frac{1}{2}$  minute for hauling. Dissolved oxygen, salinity and temperature determinations were made at each position on samples of water from a depth of 6 ft.

During the last six months of the plankton surveys, hauls with the tow-net were made near the bottom as well as near the surface. A medium tow-net of 50 meshes to the inch was used instead of the fine tow-net, as it was found to be more suitable for taking the copepod whose distribution was at that time being investigated. Samples of water were then taken near the bottom and near the surface instead of only at a depth of 6 ft., and the positions of sampling were 8,000 ft. apart. Surveys were also made at the time of low water, beginning at Stockton and finishing about three miles from the sea where marine plankton was usually present. Only the commoner species were identified, mainly by Mrs. O. M. Bartlett, and among these a variety of a marine copepod (*Eurytemora affinis* var. *hirundoides*) was the sole brackish water organism discovered.\* All other forms identified were fresh water species, mainly diatoms washed down from the upper river, or marine species of many types brought in from the sea.

*Eurytemora* in the samples taken with the medium net were counted, using a counting dish described by Russell and Colman<sup>(2)</sup>. The probable error of the method, determined by duplicate counts, was about 11 per cent. Consecutive hauls were made on two occasions with the fine and medium tow-nets in the same body of water. In two three-minute hauls the fine net caught 2,700, and the medium net 66,300 adult *Eurytemora*, so that the medium net had an efficiency of about 25 times that of the fine net. The factor probably varies with the amount of sediment and the actual numbers of *Eurytemora*. The mesh of the medium net is too large to retain the nauplii and most of the developmental stages, and the catches consisted almost entirely of adult or nearly adult specimens. In the fine net, however, the young stages were found, usually in considerably greater numbers than the adults.

## DISTRIBUTION OF EURYTEMORA IN THE TEES

The maximum catch of *Eurytemora* on each survey was taken in the central reaches of the Estuary, the numbers diminishing rapidly from the central reaches down towards the sea and up towards the fresh water reaches. Table 31 shows the results of eight high water and five low water surveys from August, 1931, to March, 1932, using the medium tow-net with both bottom and surface hauls.

The position and length of the stretch occupied by *Eurytemora*, both at high and low water, varied considerably, as also did the salinity of the water in which the maximum catch was obtained. A constant feature, however, was the abundance of *Eurytemora* in the bottom hauls and its comparative scarcity in the surface catches. The average numbers taken in a three-minute haul at each position for all the surveys given in Table 31, excluding a survey on 6th September, 1931, under fresh water flood conditions, are shown in Fig. 41,

\* Gurney<sup>(1)</sup> maintains that the *hirundoides* form of *E. affinis* cannot be held to be a true variety. In the present report the term is used to indicate that the form in the Tees Estuary is a physiological variety adapted to brackish water conditions (Chapter XV) and showing some of the characters of the *hirundoides* form.

which shows the approximate range of Eurytemora at high and low water. The effect of turbulence of the water in the shallower winding reaches above Stockton is seen in the larger numbers of Eurytemora taken in the surface hauls, and is reflected in the percentage of total surface to total bottom catches for all surveys,

TABLE 31—Results of Plankton Surveys with Bottom and Surface Hauls, using Medium Tow-Net, in the Tees Estuary from August, 1931, to March, 1932.

Date of Survey	Height of Tees on the gauge at Croft on the day preceding the survey  Ft. in.	Range of tide on day of survey  Ft.	Average monthly temperature of Estuary water  °C.	Stretch occupied by Eurytemora.					Total catch of Eurytemora at all stations
				Position in miles from the sea	Length	Distance from sea of maximum catch	Range of salinity of bottom waters	Salinity at position of maximum catch	
				Miles	Miles	Miles	Gm. per 1,000 gm.	Gm. per 1,000 gm.	
High Water surveys :									
6th Sept., 1931*	4 2	6.6	15	3½-10	6½	6½	0-23	21	843,000
19th Sept., 1931*	1 0	9.1	15	3 -15	12	8	0-30	25	2,953,000
7th Oct., 1931	0 9	7.4	13	7½-18½	11	15½	0-32	9	1,765,000
18th Nov., 1931	1 9	7.2	9½	5 -14	9	12½	0-30	18	1,059,000
4th Dec., 1931	5 4	9.5	7½	5-12½	7½	11	0-27	12	229,000
18th Jan., 1932	6 11	6.9	6½	6½-12½	6	11	1-27	20	5,000
16th Feb., 1932	1 10	6.2	5	9½-14	4½	12½	0-25	18	7,500
17th Mar., 1932	1 6	5.1	6	5 -15	10	14	0-26	4	950
Low Water surveys :									
28th Aug., 1931..	1 0	13.3	16	3½- 9	5½	5½	0-30	28	334,000
14th Sept., 1931	1 0	17.4	15	2½- 8	5½	3½	1-30	27	1,137,000
13th Oct., 1931	1 2	17.0	13	3 - 8	5	6	0-31	27	1,182,000
29th Oct., 1931	1 3	12.5	13	3 -11	8	5	0-31	30	1,310,000
13th Dec., 1931	1 9	13.3	7½	5 -11	6	8	0-28	17	79,000

\* Fine tow-net used. Catches of Eurytemora adjusted for comparison.

which was 12 per cent. for the high water surveys and only 3.5 per cent. for the low water surveys, when no copepods were found above Stockton. To determine whether Eurytemora remained in the bottom waters at half tide when the water was moving rapidly, hauls were made at Middlesbrough three hours after low water. No copepods occurred in the surface hauls and 24,000 Eurytemora were taken near the bottom.

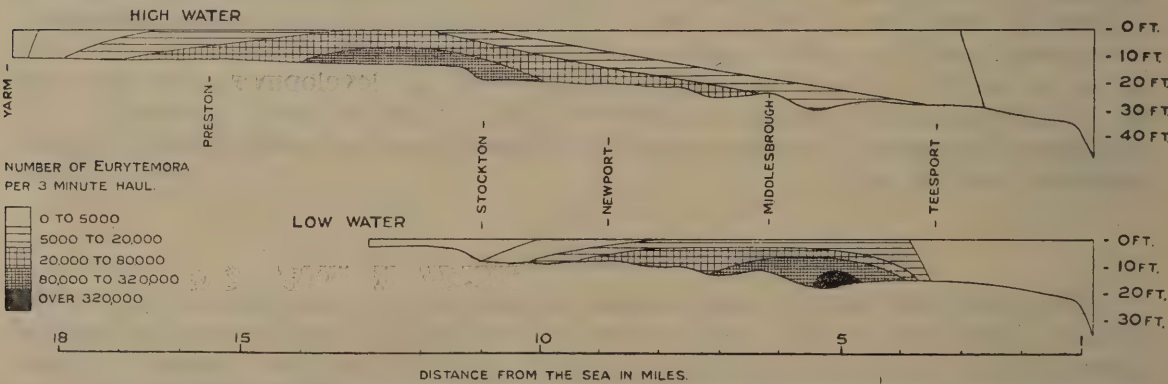


FIG. 41—Average Distribution of Eurytemora at High and Low Water in the Tees Estuary

A series of hauls was taken on a dark, moonless night on 6th November, 1931, between ½ and 2¾ hours after low water. At the four positions sampled between Middlesbrough and Newport only 8,000 Eurytemora were taken at the surface and 608,000 at the bottom, indicating that even at night, when in the sea many planktonic forms ascend to the surface<sup>(3)</sup>, the Eurytemora in the Tees remain near the bottom. The range of salinity of the waters occupied by Eurytemora is similar during the summer and winter (Table 31), although the stretch of river in which they occur is considerably shorter on some occasions in winter than in summer. The shortening is probably produced by the greater amount of water entering the Estuary during the winter from the upper river, since the bottom



waters of high salinity are comparatively stable in position and the stretch of water of low salinity is pushed downstream. Although in general occupying a similar stretch in both winter and summer, *Eurytemora* is considerably more abundant in summer than in winter. Females with egg sacs were taken during the winter months, and the reduction in the number of *Eurytemora* is probably consequent on a reduced rate of breeding brought about by the low temperature (Table 31).

During a very large flood from the upper river it seems probable that estuarine plankton is in danger of being completely washed out to sea. On 6th September, 1931, the Tees Estuary was in a much more flooded condition than the height on the Croft gauge indicates, and the surface waters even at the mouth were only very slightly brackish. The bottom waters were, however, not greatly affected. The limit of penetration of salt water was at Newport, some distance seaward of its usual high-water position. Below Newport, however, the salinity of the bottom waters rose rapidly, and it was in these waters that the main *Eurytemora* population was found, some distance below its usual position, but still  $6\frac{1}{2}$  miles from the sea.

Although of rare occurrence *Eurytemora* is occasionally found in fresh water beyond the limit of salt water penetration and on two occasions was found as high as Yarm. In an experiment with a canvas float moving with the water at a depth of 9 ft. (Chapter III) it was found that, starting at low water in a salinity of 12.2 gm. per 1,000 gm. the float moved up to Preston and was then in water of a salinity of 0.2 gm. per 1,000 gm. During the last part of the course the salinity of the water both at the surface and at the bottom was reduced from 1 to 0.2 gm. per 1,000 gm. It seems possible, therefore, for part of the *Eurytemora* population, if present at low water in water of a salinity of 5 gm. per 1,000 gm. or less, to reach at high water a stretch of fresh water some little distance above the salt water limit. It is not known whether this mechanism would account for the penetration of *Eurytemora* for more than a mile beyond the salt water limit, where it was found on two occasions.

EURYTEMORA IN OTHER ESTUARIES

A survey of the plankton was made at high water in the Firth of Tay on the 1st and 2nd June, 1932, in a manner similar to that employed on the Tees. The polluted Tyne estuary, which was known to contain *Eurytemora hirundoides*<sup>(4)</sup> was also surveyed on 20th November, 1931, two days after a similar survey of the Tees. The results of these three surveys are shown in Fig. 42. Both the Tyne and Tees estuaries are confined between narrow banks and have dredged channels

TABLE 32—*Current Measurements and Salinity Determinations in the Firth of Tay*  
June, 1932. Range of tide : 19 ft. 2 in.

Hours after low water at Dundee	Current Speeds				Salinity Determinations			
	17½ miles from the sea		12 miles from the sea		17½ miles from the sea		12 miles from the sea	
	Miles per hour		Miles per hour		Gm. per 1,000 gm.		Gm. per 1,000 gm.	
	Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom
1¼	0.6	0.3	1.6	1.4	0.4	0.4	11.3	12.2
1½	1.3	0.8	1.8	1.5	—	—	—	—
1¾	1.6	0.8	1.9	1.5	0.6	0.8	—	—
2	1.4	1.0	2.0	1.5	—	—	—	—
2¼	1.6	1.0	1.8	1.3	—	—	13.9	14.2
2½	1.6	1.2	1.8	1.5	—	—	—	—
2¾	1.7	1.1	1.9	1.3	1.5	1.3	—	—
3	1.7	1.0	1.8	1.3	—	—	—	—
3¼	1.8	1.4	1.7	0.9	—	—	16.4	17.3
3½	1.9	1.3	—	—	—	—	—	—
3¾	2.1	1.5	—	—	3.2	5.0	—	—
4	2.2	1.5	—	—	—	—	—	—
4¼	2.1	1.2	—	—	6.0	7.2	—	—

for a considerable distance from the sea. The similarity of their salinity curves indicates that the residual upstream movement of the bottom water which occurs in the Tees (Chapter III) is probably found in the Tyne. In the Tay and Tamar it is probably less marked. In the Tay the vertical salinity gradient is small; current measurements show that the surface waters move more rapidly upstream on the flood tide than do the bottom waters (Table 32). The upper and middle reaches of the Tamar are shallow, almost drying out at low water. There is, however, a population of *Eurytemora* in approximately the same position in all four estuaries (Fig. 42). In the Estuary of the Tees, and in that of the Tyne,

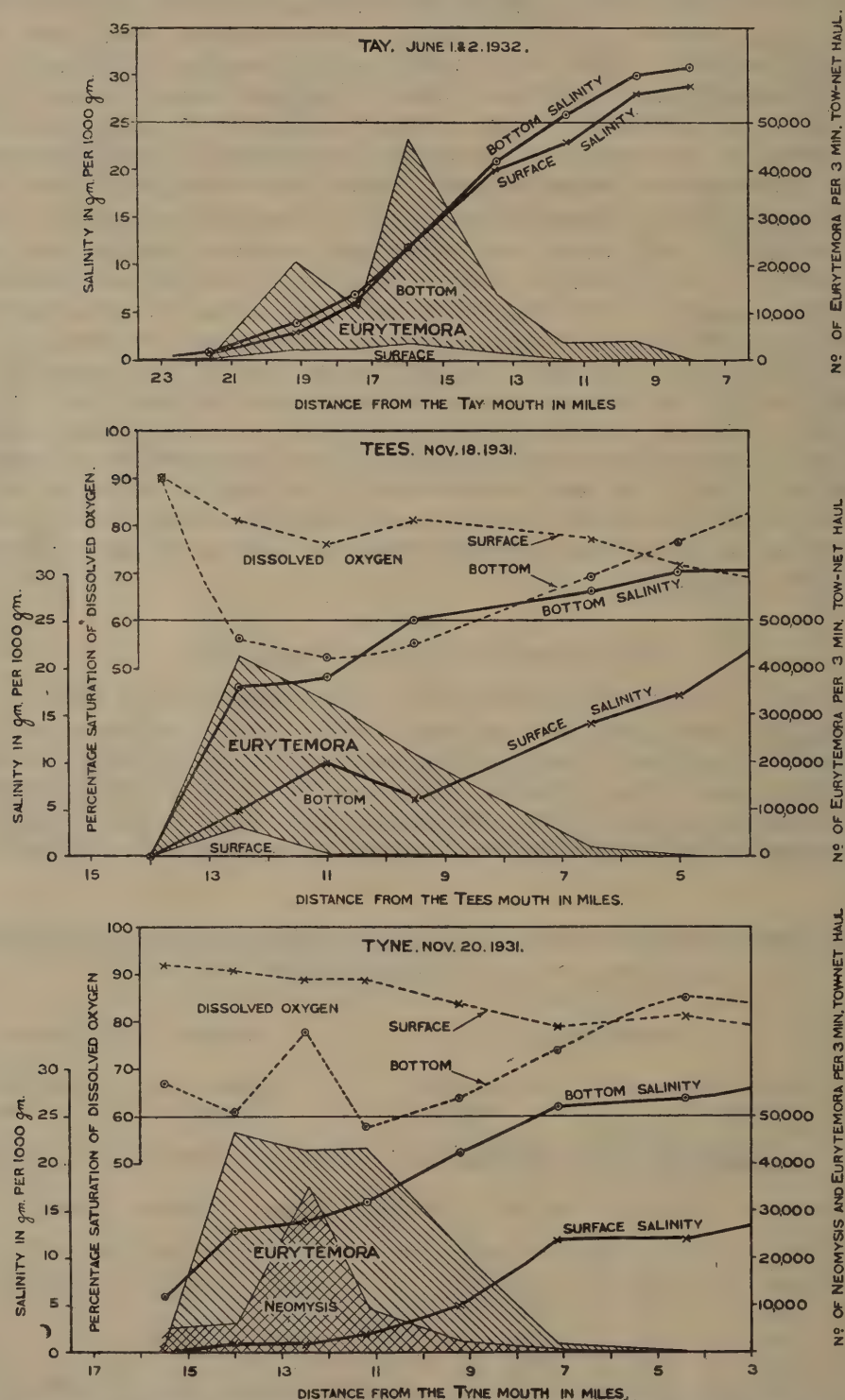


FIG. 42—Distribution of *Eurytemora* in the Estuaries of the Tay, Tees, and Tyne

the residual upstream movement of the bottom water probably helps to prevent the bottom-living *Eurytemora* from being washed out to sea. In the Tay and Tamar, however, no marked residual upstream movement of the bottom waters is indicated, hence some other mechanism probably exists in all four estuaries to maintain the brackish water plankton within the estuary.



MARINE PLANKTON IN THE TEES

Both marine and fresh water species die out on being carried into the Estuary. Marine plankton enters the Estuary in the bottom waters and fresh-water species are carried down in the surface waters (Figs. 43 and 44). The average numbers taken and the distribution of the marine diatom *Coscinodiscus* and of marine copepods are given in Table 33.

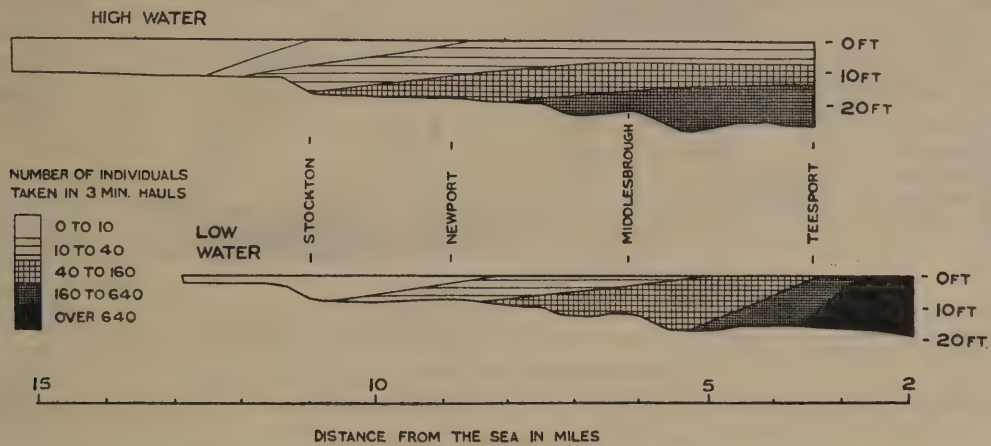


FIG. 43—Average Distribution of Marine Plankton at High and Low Water in the Tees Estuary

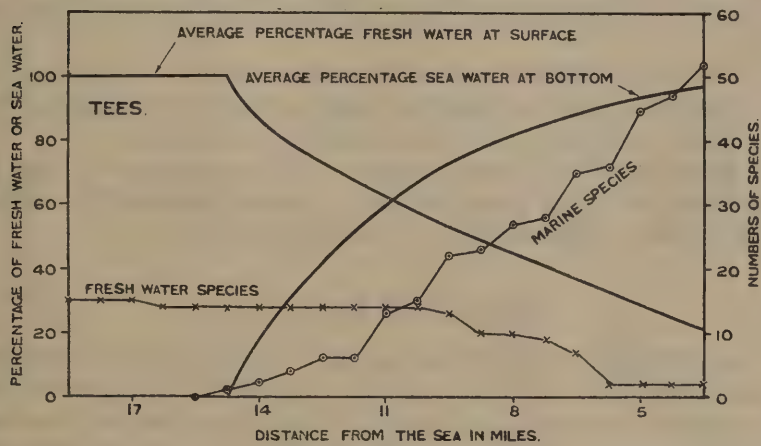


FIG. 44—Number of Planktonic Species found, and Average Percentages of Salt and Fresh Water in the Tees Estuary at High Water

TABLE 33—Average Numbers of *Coscinodiscus* and Marine Copepods Taken in Three Minute Hauls with Medium Tow-Net in the Tees Estuary.

Autumn and Winter, 1931 and 1932

Distance from the sea Miles	Coscinodiscus				Marine Copepods			
	High water		Low water		High water		Low water	
	Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom
14	0	0	0	0	1	1	0	0
12½	0	4	0	0	1	6	0	0
11	0	3	0	0	4	24	0	5
9½	0	6	0	6	12	74	0	4
8	0	10	0	0	21	125	30	0
6½	0	27	2	0	8	111	0	0
5	0	120	1	10	19	164	2	7
3½	4	108	1	30	27	262	63	370

The marine worm, *Polydora ciliata*, is abundant in the central reaches and its larvae were frequently taken in the plankton from April to October or November. Although marine, its abundance in estuaries indicates a tolerance to brackish water, probably shared by its larva. The larva had a distribution (Fig. 45) similar to that of the estuarine *Eurytemora* except that it died out above Stockton.

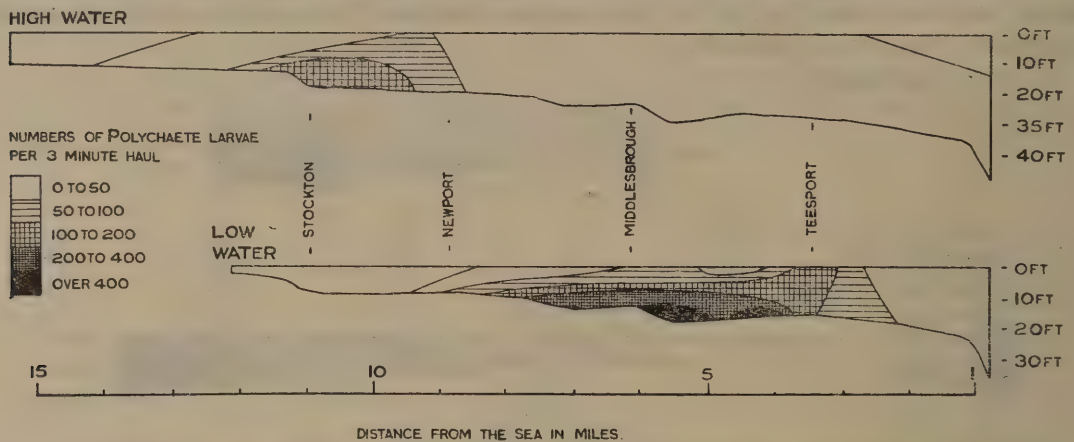


FIG. 45—Average Distribution of Polychaete Larvae at High and Low Water in the Tees Estuary

The brackish water *Eurytemora* and *Polydora* larvae, which can tolerate brackish water conditions, have a distribution entirely different from those of the fresh water and true marine planktonic species. It seems possible, therefore, that the distribution of the two estuarine species is imposed on them by the current system of the Estuary.

The results of the plankton surveys in the estuaries of the Tyne and Tay show that, as in the Tees, the marine plankton enters the Estuary mainly in the bottom waters and dies away gradually as the estuary is ascended.

On many occasions living individuals of *Eurytemora* in the Tees Estuary have been observed to carry growths of a colonial vorticellid. Similar growths have been observed on *Eurytemora* from the Firth of Tay.

#### EFFECTS OF POLLUTION

From the abundance of *Eurytemora* and the presence of *Polydora* larvae in the most polluted reaches of the Estuary of the Tees it appears that the pollution has very little effect on these organisms. The lack of variety of brackish water planktonic species is no indication of pollution since in the Firth of Tay a similar dearth was observed.

On two occasions a scarcity of *Eurytemora* occurred in the reaches between Middlesbrough and Stockton, but from the rarity of this occurrence it seems that it is not an effect of the normal pollution. Dead *Eurytemora* were occasionally abundant in plankton samples, but they seemed to be individuals from the main population being washed down the Estuary and were probably not killed by pollution. In Chapter XV it is shown that the concentrations of poisons occurring in the Tees Estuary have no effect on *Eurytemora* in a period of a few days.

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## CHAPTER XI

TOXICITY OF EFFLUENTS : RAINBOW TROUT (*SALMO IRIDEUS* GIBB)  
AS TEST ANIMALS

In investigating the comparative polluting effects of the different discharges into the Estuary, test fish have been used under standard conditions as indicators of toxicity. The most valuable fishery of the Tees is that of salmon and sea trout, and it is this fishery which is chiefly affected by pollution, since both immature and adult fish are killed during migration to and from the sea. It has been shown by many workers that the susceptibilities of different types of fish to poisons and to oxygen deficiency are not the same. Thus, the resistance of the rainbow trout to poisoning by tar has been shown by Hein<sup>(1)</sup> to be less than that of the stickleback and there is a marked difference in the susceptibility of three American fish, the Darter, Rock Bass and Catfish, to poisoning by cyanides<sup>(2)</sup>. A considerable amount of work has been done on the resistance of different types of fish to low concentrations of dissolved oxygen. Gutsell<sup>(3)</sup> has shown that the American rainbow trout (*Salmo shasta*) and the brown trout (*Salmo fario*) are more susceptible to oxygen deficiency than the American brook trout (*Salvelinus fontinalis*). Gardner<sup>(4)</sup> found that the brown trout (*Salmo trutta*) was unable to withstand such low concentrations of oxygen as the coarse fish, pike, eel and goldfish. Krogh and Leitch<sup>(5)</sup> correlated the minimum oxygen concentration required by different fish with the properties of their haemoglobin, and showed that in coarse fish, such as the carp, eel and pike, which may be exposed to water of low oxygen content, the blood is saturated with oxygen at a relatively low pressure. In marine fish and in fish such as the trout, which normally live in well oxygenated water, the oxygen tension at which the blood is saturated is considerably higher.

It was to be expected that salmon and sea trout smolts, which normally inhabit swiftly flowing, well oxygenated streams, would be highly susceptible to dissolved oxygen deficiency and possibly to direct poisons. Owing to the difficulty of obtaining regular supplies of smolts, however, it was decided to use small trout as test fish since their habitat and general characteristics are similar to those of smolts. Brown trout (*Salmo trutta*) were not so suitable for the experimental work, since when placed in toxic solutions they normally lay on the bottom of the experimental vessel on their pectoral fins, sometimes even up to and after their death; a similar observation has been made by Roberts and Jee<sup>(6)</sup>. Rainbow trout (*Salmo irideus*), which were used as test animals throughout the present investigation, were found to be much more active, and the point at which they lost their equilibrium in toxic solutions was well marked. From the few observations made the susceptibility to poisons of rainbow trout and of salmon and sea trout smolts appears to be of the same order. A few comparisons are given in Table 34. Figures given for the length of time before the fish overturned are the means of several determinations, the numbers of which are given in brackets; in the case of rainbow trout the times, when the number of determinations is not given, are the averages of a large number of observations made at different periods of the survey.

TABLE 34—*Comparative Susceptibility to Poisons of Salmon and Sea Trout Smolts and Rainbow Trout*

Number of determinations in brackets

Average time of overturning Minutes		Poison Gm. per 100 litres
Smolts	Rainbow trout	
20 (11)	11	Cyanide (CN)
13½ (8)	9½	0.02
8 (4)	9 (2)	0.03
6 (12)	6 (2)	0.04
		0.075
20 (4)	100	Phenol
5½ (4)	13 (2)	0.8
		0.9

## METHOD OF TESTING

In the determination of the toxicity of a solution by its effect on fish, it is usual to observe the time interval between the exposure of the fish and the onset of some easily recognised symptom of poisoning. The behaviour of trout differs widely in different poisons. In solutions of phenolic substances, for example, they usually become very active, dashing about and repeatedly losing and recovering their equilibrium. In solutions of cyanides trout usually remain quiet, finally overturning in a helpless condition without any previous loss of balance. In all cases in toxic concentrations of poisons, they finally overturn and are unable to regain their normal swimming position. The length of time between the first exposure of the fish and this final overturning point has been taken as a measure of the toxicity of the tested solutions. If allowed to remain in a toxic solution after having overturned, a fish usually dies within a short time, but in the cases of tar acids and potassium cyanide it generally recovers if removed immediately after overturning and placed in clean water. The actual survival time of fish in toxic solutions has been observed by some workers, but the determination of the exact time of death is somewhat difficult. Powers <sup>(7)</sup> recommends the placing of apparently dead fish in dilute hydrochloric acid, when movement usually occurs if they are still alive.

The toxicity of a solution is proportional to the reciprocal of the survival time, and is here represented by the value  $\frac{100}{t}$ , where  $t$  is the time in minutes taken for the fish to overturn.

## STORAGE OF STOCK FISH

No difficulty was found in maintaining a stock of trout in the tap water supplied to the laboratory. The fish were kept in a large iron tank lined with cement, and the water was continuously renewed and aerated. Occasionally a few fish were attacked by fungus and were discarded. Trout appear to be more susceptible to the effects of poisons immediately after feeding and were therefore not used until about 12 hours after a meal.

## SIZE OF FISH

It has been stated by Steinmann and Surbeck <sup>(8)</sup> that the fry of Salmonidae are very resistant to the effect of phenol, a result which has been confirmed by Gardiner <sup>(9)</sup>. During the survey the trout used were 1 to 2 years old and approximately 2 to 4 inches in length; fish of a larger size than this were discarded.

## EXPERIMENTAL CONDITIONS

In comparing the toxicity of direct poisons, it is important that the experimental solutions should be well oxygenated, at approximately the same temperature and of the same reaction or pH value.

It is generally supposed that the toxicity of a solution of a poison is increased as its dissolved oxygen concentration is lowered, although no experimental evidence in support of this view has been found in the literature. Some experiments were carried out in which the toxicities of potassium cyanide and *p*-cresol when diluted with partially de-aerated tap water were determined. A supply of deoxygenated water was obtained by a method similar to that described by Shelford <sup>(10)</sup>. Water was boiled for some hours in open vessels and cooled in completely full, airtight, galvanised iron cans. When cold, carbon dioxide was bubbled through the water until the pH fell to approximately 7.0. By this method water containing a concentration of oxygen equivalent to about 5 per cent. of the saturation value could be obtained. For experimental purposes this water was brought to the required oxygen concentration either by aeration or by mixing with tap water. It was found, in a series of experiments, that the toxicities of cyanide solutions of the same concentration were the same whether they were made up with boiled and re-aerated water or with tap water. Solutions containing 0.62 gm. *p*-cresol or potassium cyanide equivalent to 0.011 gm. (CN) per 100 litres were made up with water containing dissolved oxygen in various concentrations and the toxicities to rainbow trout were determined. With low concentrations of oxygen the experiments were carried out in stoppered carboys containing about 20 litres of solution and one or two fish were used; at higher oxygen concentrations open



vessels containing 30 litres and usually five fish were employed. The oxygen concentration did not vary appreciably during any experiment.

The relation between the toxicity of a cyanide solution and the oxygen concentration is shown in Fig. 46. For each 10 per cent. rise in oxygen concentration, 20 determinations of toxicity were made and in each group the oxygen values and toxicities were averaged for each point on the graph. As the concentration of oxygen was lowered the toxicity of the cyanide increased. The relation between the extent of oxygenation and the toxicity of a *p*-cresol solution (Fig. 47) is similar to that for potassium cyanide. The curve for *p*-cresol is based on eight determinations of toxicity for each 10 per cent. rise in oxygen concentration.

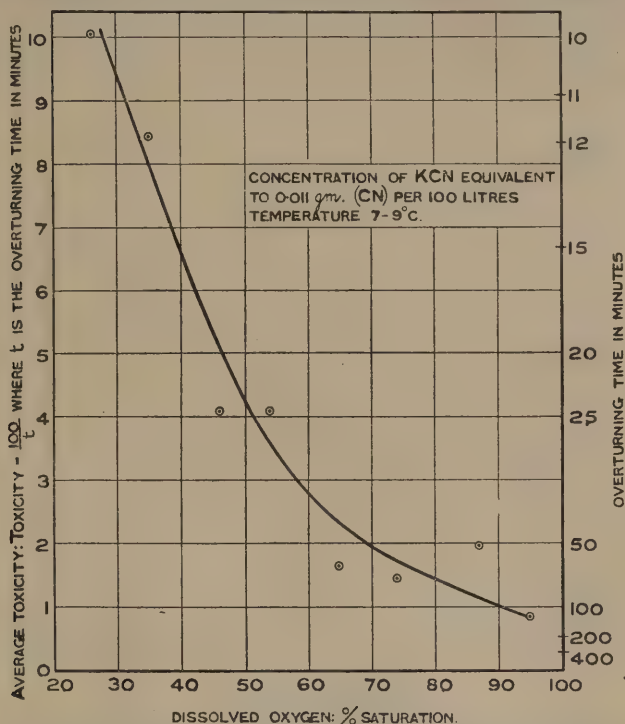


FIG. 46—Toxicity to Rainbow Trout of Potassium Cyanide in Solutions of Different Dissolved Oxygen Concentrations

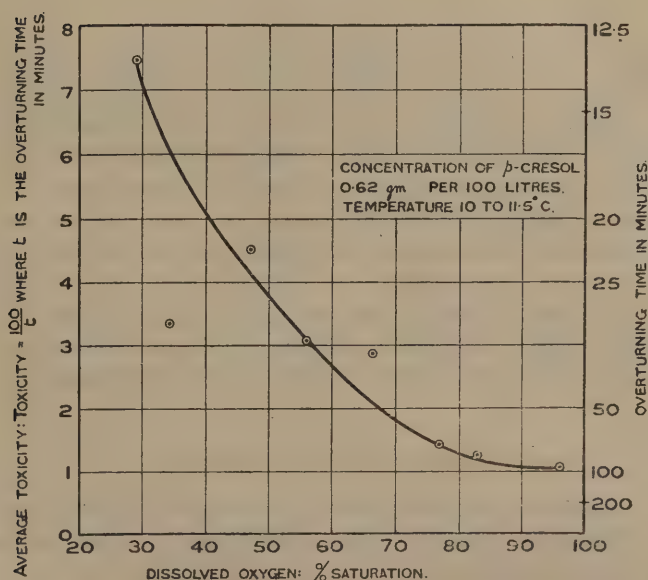


FIG. 47—Toxicity to Rainbow Trout of *p*-Cresol in Solutions of Different Dissolved Oxygen Concentrations

In all determinations of toxicity the dissolved oxygen concentration was determined at the time of placing the fish in the experimental solution, and, in the longer period experiments, again when the fish were removed. As large volumes of solution were used the dissolved oxygen concentration was not lowered

materially by the respiration of the fish. In the experiments described in the following paragraphs all toxicity determinations, unless otherwise stated, were carried out on solutions approximately saturated with dissolved oxygen.

The toxicity of solutions of potassium cyanide was found to increase rapidly with rise in temperature (Fig. 48). Each point on the graph is the mean of about four determinations. The temperature variation during any determination did not exceed  $0.5^{\circ}\text{C}$ . In view of the considerable influence of temperature on the toxicity of potassium cyanide, all experiments in any one series were carried out at about the same temperature. Colorimetric determinations of the pH value of solutions of all substances under examination were made, and the reaction was adjusted to neutrality where necessary by the addition of hydrochloric acid or sodium hydroxide. In general, such adjustment was required only in experiments with industrial effluents.

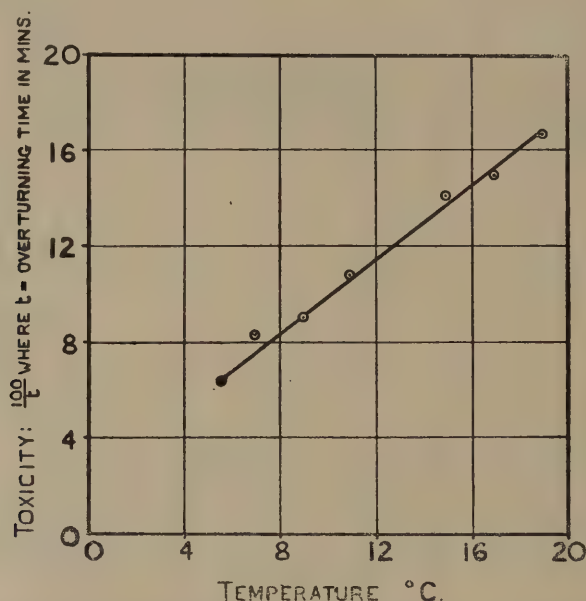


FIG. 48—Relation between the Toxicity to Trout of a Solution of Potassium Cyanide (0.03 gm. (CN) per 100 Litres and the Temperature

#### SALINITY

In the determination of the toxicity of effluents and of solutions of pure substances, fresh water was used as diluent. In tests of the toxicity of Estuary water, however, the effect of salinity on the fish was of importance.

It has been shown by Meek<sup>(11)</sup> that yearling brown trout are fairly resistant to the effects of water of high salinity, living in some cases for several days in undiluted sea water. During the Tees survey it was found that rainbow trout lived comfortably in water of salinity not greater than 27.5 gm. per 1,000 gm. for periods up to 24 hours, the longest time for which they were exposed to test samples of Estuary water. In unpolluted water of a salinity greater than 27.5 gm. per 1,000 gm. trout occasionally died after exposure for some hours. In the majority of samples of Estuary water tested, the salinity was considerably below this value.

#### ACCURACY OF RESULTS

The accuracy with which the toxicity of a solution can be determined varies considerably with different poisons. The variations in the value for the toxicity of a given solution as determined by the overturning times of trout arise partly from the different susceptibilities of individual fish and often from the difficulty of determining the overturning point. With cyanide the overturning point is definite, but with solutions of phenolic substances trout may lose and regain their equilibrium several times before finally remaining in an overturned position.

The variation in the susceptibility of trout to solutions of potassium cyanide and some phenolic substances is shown in Table 35. The variability among comparable groups of determinations generally increased with increasing dilution of the poison.



TABLE 35—*Variation in Susceptibility of Rainbow Trout to Different Poisons*

Concentration of poison as percentage of maximum concentration used.	Coefficient of variation= $\left(\frac{100 \times \text{Standard deviation}}{\text{Arithmetic mean}}\right)$			
	Potassium cyanide (Maximum concentration : 0.042 gm. (CN) per 100 litres)	<i>p</i> -Cresol (Maximum concentration : 0.83 gm. per 100 litres)	Phenol (Maximum concentration : 1.0 gm. per 100 litres)	1.2.6. Xylenol (Maximum concentration : 1.5 gm. per 100 litres)
100	8	30	54	51
90	8	19	69	71
80	10	41	110	68
70	12	74	33	122
60	14	70	—	214
50	19	—	—	100
40	33	—	—	—
30	52	—	—	—
Number of determinations at each concentration	10	20	20	10

The standard deviation ( $\sigma$ ) is defined by the relation

$$\sigma^2 = \frac{\text{Sum of } d_1^2 + d_2^2 \dots + d_n^2}{n}$$

where  $d_1, d_2$ , etc., are the differences between individual determinations and the arithmetic mean.

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## CHAPTER XII

## TOXIC SUBSTANCES DISCHARGED INTO THE ESTUARY

During the survey the positions of the outfalls between Stockton and Cargo Fleet discharging sewage and industrial effluents were determined and the principal effluents were investigated. In all, 144 discharges, of the types shown in Table 36, were examined. The work described in this Chapter consisted of an examination of the toxicities of the more important of these effluents and their main groups of constituents. Experiments included in the work on the non-tidal reaches of the River Tees showed that under aerobic conditions crude sewage in concentrations such as are found in the Estuary is not directly toxic to fish. Very large quantities of water are taken from the Estuary and used for the cooling of condensers and similar purposes. When returned to the Estuary this water is often contaminated with small quantities of oil and grease and its oxygen content may have been lowered, but it contains no directly toxic substances.

TABLE 36—*Nature of the Main Discharges Entering the Tees Estuary*

Type of discharge	Number of outfalls
Sewage from domestic sources ... ..	49
Sewage from industrial works ... ..	27
Land drains ... ..	22
Condenser cooling water ... ..	20
Coke oven effluents ... ..	12
Spent pickle liquor ... ..	6
Grain washing water ... ..	1
Miscellaneous ... ..	7

## SPENT PICKLE LIQUORS

These effluents are produced during the manufacture of galvanised sheet and wire. Before galvanising, the steel sheets are cleaned in hydrochloric acid, fresh acid being added from time to time as the cleaning proceeds. Finally, the spent acid is discharged and a fresh bath prepared, usually at the end of each shift. The discharge of pickle effluents is thus intermittent. Their composition varies considerably at different works and at different times, but the main constituents are ferrous iron, some ferric iron, and free hydrochloric acid. The following figures refer to samples taken from two of the larger plants :

	Per cent.	Per cent.
Total iron .. ..	16·1	17·7
as ferrous iron .. ..	15·7	17·6
as ferric iron .. ..	0·4	0·1
Free acid as HCl .. ..	3·1	1·3

The output of spent pickle acid varies widely according to trade conditions. It was estimated that in 1929 effluents containing roughly 7 tons of ferrous iron were discharged daily.

It appears that the ferrous salts are fairly rapidly oxidised and precipitated in the Estuary, and this view is supported by the fact that soluble iron has never been detected in samples of the Estuary water collected at some distance from the points of discharge. A few experiments were carried out to determine the rate of precipitation. To 1 litre of Estuary water in a stoppered bottle was added ferrous sulphate equivalent to 7 mg. Fe per litre to give a mixture comparable with that in the Estuary. At intervals samples were withdrawn and filtered, the ferric precipitate was dissolved in dilute acid and the ferric iron in the resulting solution



was determined colorimetrically. The following figures give the time necessary for 80 per cent. of the added iron to be precipitated in various samples of Estuary water :

<i>Estuary water</i>		<i>Time for precipitation of 80 per cent. of added iron</i>
Salinity	pH	(mins.)
33.4	8.4	10
30.9	8.2	18
14.5	7.5	33

The free hydrochloric acid discharged does not normally cause any marked increase in the acidity of the general body of the Estuary waters. Spent pickle liquors, therefore, are not thought to have any directly toxic action on fish under the conditions and in the quantities in which they are discharged.

#### EFFLUENTS FROM COKE OVENS

Discharges from coke ovens, though comparatively few in number, constitute by far the most important source of toxic material entering the Estuary. With the exception of a few of comparatively minor importance, all these discharges arise from processes concerned with the cooling and scrubbing of coke oven gas and the recovery of ammonia. It is of interest, therefore, to consider briefly the processes of coke oven gas treatment adopted in the Tees area.

In all types of plant the most important by-products recovered are tar, ammonia, naphthalene and benzol. The method of recovery of tar and benzol are similar at the different works, but ammonia is recovered by either the direct or the semi-direct process. At the time when the work described was carried out, there were in operation three semi-direct and two direct process plants.

In the direct method of ammonia recovery, as adopted at the coke ovens on the banks of the Tees Estuary, the crude gas passes through a tar extractor where tar is removed at a temperature of 65° to 70° C. before the liquor condenses; the hot gas then passes through a saturator in which the ammonia is absorbed in sulphuric acid and recovered as ammonium sulphate. The gas, after leaving the saturator at a temperature of about 70° C., is cooled, before passing to the benzol recovery plant, by direct contact with a large volume of water pumped from the Estuary and sprayed into the gas in a series of tall cooling towers. The effluent contains soluble material washed from the gas together with a suspension of naphthalene and some light oil. Part of the naphthalene is removed at the base of the cooling towers and part in a settling tank through which the effluent flows before being discharged into the Estuary.

In those coke oven installations on the banks of the Estuary in which the semi-direct process of ammonia recovery is employed, the gas leaving the coke ovens is cooled in condensers to about 25° C., when liquor and tar containing naphthalene in solution separate out. The liquor is separated from the tar and distilled with lime; the distillation gases are then mixed with the coke oven gas and passed through a saturator for the recovery of ammonium sulphate. The spent liquor from the ammonia still constitutes one of the effluents from this type of process, and is discharged without further treatment into the Estuary, except in one plant in which it is used for coke quenching. After leaving the saturator at a temperature of about 70° C., the gas is cooled as in the direct process before benzol recovery. In two plants the cooling is effected in indirect condensers, in which case the condensate is mixed with the ammonia liquor before distillation and no further effluent is produced. In a third plant, cooling is carried out by direct contact of the gas with Estuary water in a series of towers, and the effluent, after the removal of naphthalene, is discharged into the Estuary. The composition of this effluent is approximately the same as that produced in the corresponding cooling system of the direct process.

The waste liquors from ammonia recovery plant are, therefore, of two types : (1) gas cooling and washing effluents from both direct and semi-direct processes, consisting of water which has been used to cool the gases at a point between the ammonia saturator and the benzol recovery plant. The production of this effluent is avoided in plants where indirect cooling is employed. The volume of effluent discharged from the direct coolers in the plants under consideration varied from about 1,000 gallons to 1,400 gallons per ton of coal carbonised; and (2) spent still liquor from semi-direct process installations. The volume of this effluent depends partly on the moisture content of the coal carbonised, and is stated to vary from 45 gallons to 50 gallons per ton of coal.

*Effluents from Gas Coolers*

Analyses of samples of effluents from gas cooling towers of coke oven installations are given in Table 37. Effluents Nos. 59 and 31 were each discharged in average volumes of about one million gallons in 24 hours. These effluents were from unpacked cooling towers into which Estuary water was sprayed through a number of nozzles. Effluent No 10, with an average volume of 630,000 gallons in 24 hours, was from towers packed with wooden grids over which Estuary water was allowed to flow. The volumes discharged varied considerably from time to time.

TABLE 37—*Composition of Effluents from Coke Oven Gas Coolers*

	Effluents from coolers following direct ammonia recovery		Effluent from coolers following semi-direct ammonia recovery
	*No. 59	No. 31	No. 10
Part per 100,000—			
Alkalinity equivalent to CaO ...	14	16.8	10.1
Ammonia, free ... ..	3	—	—
Ammonia, fixed ... ..	2	—	—
Thiocyanate ... ..	Nil	—	—
Thiosulphate as S ... ..	7	—	—
Cyanide as HCN ... ..	4	8.0	8.2
Chlorine as HCl ... ..	16.5	12.0	6.1
Sulphur as H <sub>2</sub> S ... ..	Trace	—	—
Monohydric phenols as C <sub>6</sub> H <sub>5</sub> OH	10.5	—	—
Total tar acids ... ..	12.5	13.0	6.3
Oxygen consumed from N/80 permanganate at 80° F.			
In 4 hours ... ..	57.0	—	25.6
In 3 minutes ... ..	20.0	—	—

\* Analysis by the Government Chemist.

Large variations in the composition of the effluents also occur, especially in the concentrations of alkali and sulphide. The concentration of sulphide depends largely on the quantity of ammonia which leaves the ammonia saturator. Since the addition of sulphuric acid is intermittent, the efficiency of the saturator decreases as the charge of acid is gradually neutralised. The cyanide and tar acid contents of the effluents are less liable to variation. In Table 38, the variations in composition of 26 samples of Effluent No. 31, taken at intervals of from 1 to 4 days, are shown. At one works the manufacture of ammonium sulphate was discontinued during a period of several weeks. Under these conditions the average sulphide content increased from 7.7 to 49 parts of H<sub>2</sub>S per 100,000, and the alkalinity from 11.8 to 83 parts of CaO per 100,000. The concentrations of cyanide and tar acids were not appreciably affected.

TABLE 38—*Composition of Effluent No. 31 from Gas Coolers*  
26 Samples Examined

	Mean values parts per 100,000	Maximum percentage variation from mean
Alkalinity equivalent to CaO	11.8	+147 — 76
Sulphide as H <sub>2</sub> S	7.7	+165 — 78
Cyanide as (CN)	7.8	+ 15 — 20
Total tar acids	13.0	+ 15 — 31



Effluents from coke oven gas coolers were found to be highly toxic to trout. They were examined by various methods, using trout as indicators of toxicity, with the object of identifying their main poisonous constituents. When distilled in neutral solution the distillate was always of approximately the same toxicity as the original effluent; the poisonous substances were therefore volatile. The constituents were then separated into the main groups of basic plus neutral and acid plus neutral substances, by distillations from alkaline or acid solution, and the toxicity of these groups was determined. Representative results are given in Table 39. The results show that :—(1) basic substances do not contribute appreciably to the toxicity of the effluent, (2) neutral volatile bodies, which would distil over either in acid or alkaline solution, are not an important toxic factor, and (3) the main toxic constituent is of an acidic nature.

TABLE 39—*Toxicity of Different Fractions of Effluents from Gas Coolers*

Effluent	Volume diluted with water to 100 volumes	Effluent or Fraction	Effect on rainbow trout in 30 min.
No. 59 Sample 1	2	Untreated effluent	Toxic
	2	Distillate from acid solution	Toxic
	2	Distillate from alkaline solution	Non-toxic
No. 59 Sample 2	1	Distillate from alkaline solution	Non-toxic
	1	Residue distilled from acid solution	Toxic
	1	Distillate from acid solution	Toxic
	1	Residue distilled from alkaline solution	Non-toxic
No. 31	2	Untreated effluent	Toxic
	2	Distillate from acid solution	Toxic
	2	Distillate from alkaline solution	Non-toxic

An aqueous solution (A) was then prepared by dissolving pure substances in the following proportions in water :—

	Parts per 100,000.
Sodium chloride .. .. .	2,730
Sodium thiosulphate .. .. .	34
Ammonium chloride .. .. .	9
Phenol .. .. .	10.5
Mixed xylenols .. .. .	2
Potassium cyanide .. .. .	10

This mixture contained the main constituents of Effluent No. 59 in the concentrations shown in Table 37. The toxicity of the mixture was approximately the same as that of the effluent. A series of solutions was then made up of the same composition as Solution A, except that each constituent was in turn omitted. It was found that the toxicity of each solution was approximately the same as that of Solution A, except when potassium cyanide was omitted, when a 1 per cent. solution of the mixture was non-toxic under the conditions of the experiment. Moreover, a solution of potassium cyanide of a concentration equivalent to that in which cyanide occurs in Effluent No. 59 was of approximately the same toxicity as the effluent.

The cyanide in effluents from the washing of coke oven gas with water was removed by the addition of silver nitrate, after which 1 per cent. solutions of the effluents were innocuous to trout. The chloride content of the effluent was first determined, and an excess of silver nitrate added to precipitate both chloride and cyanide. After filtration, sufficient sodium chloride was added to precipitate excess silver nitrate and restore the chloride concentration to its original value.

The precipitate of silver chloride was filtered off and the toxicity of the filtrate determined. This treatment had no effect on the toxicity of a solution of phenol, but cyanides were completely removed from solution (Table 40).

TABLE 40—*Effect of Treatment with Silver Nitrate on the Toxicities of Solutions of Phenol and of Potassium Cyanide*

Concentration in solution treated	Effect of 1 per cent. solution on trout
Phenol. 200 gm. phenol per 100 litres.	Before treatment— toxic in 3 minutes. After treatment— toxic in 3 minutes.
100 gm. phenol per 100 litres.	Before treatment— toxic in 7 minutes. After treatment— toxic in 8 minutes.
KCN. 10 gm. (CN) per 100 litres.	Before treatment— toxic in 8 minutes. After treatment— non-toxic in 18 hours.

A second method of cyanide removal used consisted in adding to the effluent a small quantity of formaldehyde which with cyanides forms cyanhydrin, a compound comparatively innocuous to fish (Appendix II). The addition of formaldehyde to effluents from gas coolers following direct ammonia recovery rendered the effluents non-toxic in concentrations up to 2 per cent. The reduction in toxicity brought about by the removal of cyanides with either silver nitrate or formaldehyde is shown in Table 41. It is evident that cyanide is the chief toxic constituent of effluents from coke oven gas coolers.

TABLE 41—*Effect of Removal of Cyanide on Toxicity of Effluents from Gas Coolers*

No. of effluent	Concentration per cent.	Toxicity to trout over 2 hour period		
		Untreated	Silver nitrate treatment	Formaldehyde treatment
31	1	Toxic in 8 min.	Non-toxic	Non-toxic
31	2	Toxic in 4 min.	Non-toxic	Non-toxic
59	1	Toxic in 6 min.	Non-toxic	—
59	$\frac{3}{4}$	Toxic in 9 min.	—	Non-toxic
10	5 per cent. of effluent previously diluted with cooling water at the works.	Toxic in 8 min.	—	Non-toxic

### *Spent Still Liquors*

Results of analyses of typical samples of the spent still liquors discharged into the Estuary from two semi-direct process ammonia recovery plants are shown



in Table 42. Effluent No. 1A was discharged into a ditch which had no obvious outlet to the Estuary.

TABLE 42—*Composition of Spent Still Liquors from Semi-Direct Process Ammonia Recovery Plants*

Effluent No.	1A*	159*
Parts per 100,000 :—		
Alkalinity, equivalent to CaO .. ..	170	200
Ammonia, free .. .. .	29	24
Ammonia, fixed .. .. .	3	3
Thiocyanate as CNS .. .. .	11	10
Thiosulphate as S .. .. .	23	27
Cyanide .. .. .	Nil	Nil
Chlorine as HCl .. .. .	191	158
Sulphide as H <sub>2</sub> S .. .. .	Trace	Trace
Monohydric phenols as C <sub>6</sub> H <sub>5</sub> OH ..	163	184
Total tar acids .. .. .	200	250
Oxygen consumed from N/80 perman- ganate at 80° F. :		
In 4 hours .. .. .	445	494
In 3 minutes .. .. .	293	315

\* Analyses by the Government Chemist.

The general nature of the toxic constituents was examined by means of a series of distillations similar to those carried out with gas cooling effluents. Typical results are shown in Table 43.

TABLE 43—*Toxicity of Different Fractions of a Spent Still Liquor (No. 159)*

Volume diluted with water to 100 volumes	Effluent or Fraction	Effect on rainbow trout
1	Untreated effluent .. .. .	Toxic (6 min.)
1	Distillate from acid solution ..	Toxic (5 min.)
1	Distillate from acid solution after H <sub>2</sub> S removal.	Toxic (4 min.)
1	Distillate from alkaline solution	Non-toxic (30 min.)
2	Untreated effluent .. .. .	Toxic (3 min.)
2	Distillate from acid solution ..	Toxic (3 min.)
2	Distillate from alkaline solution	Non-toxic (30 min.)

A 1 per cent. solution of another effluent of the same general composition as that shown in Table 42 was toxic to trout in about 6 to 10 minutes. The toxic constituents were volatile and could be distilled from acid or neutral but not from alkaline solution. Removal of the sulphide by precipitation as lead sulphide did not appreciably affect the toxicity. No change in toxicity was brought about by treating the effluent with formaldehyde or with silver nitrate. A solution of a cresol or phenol in the same concentration as that of the tar acids in the effluent had about the same toxicity as the effluent. It is concluded, therefore, that the tar acids are the main toxic constituents of spent still liquor from semi-direct process ammonia recovery plants.

Other important effluents similar in character to coke oven effluents were also examined, and the toxicity of their main groups of constituents was determined. For example, Effluent No. 11 from a tar and benzol works gave on analysis the results in Table 44. The concentration of free acid in this effluent was high. Observations showed, however, that no appreciable alteration of the hydrogen ion concentration of the general body of the Estuary waters was brought about by the effluent in the quantities discharged and the toxicity due to its

acid content was therefore not investigated. The pH values of solutions of the effluent, or of fractions of it used for toxicity determinations, were raised approximately to neutrality by the addition of soda. In Table 45 the toxicities of the effluent and of distillates obtained in various ways are shown. The toxicity of the effluent was mainly due to constituents which could be distilled from acid solution, but, unlike coke oven effluents, there was also an appreciable toxicity due to basic substances. Volatile neutral bodies did not appreciably add to the toxicity. No change in the toxicity of this effluent was brought about by treatment with formaldehyde or silver nitrate.

TABLE 44—*Effluent from Tar and Benzol Works*

Sample No.	1	2
Parts per 100,000 :—		
Cyanides .. .. .	0	0
Total tar acids .. ..	42·5	20
Free acid, as H <sub>2</sub> SO <sub>4</sub> ..	—	232
Oxygen consumed from N/8 permanganate at 80°F. in 4 hours.	217·5	142·8

TABLE 45—*Toxicity of Various Fractions of Effluent from Tar and Benzol Works*

Volume diluted with water to 100 volumes	Effluent or Fraction	Effect on rainbow trout
1	Untreated effluent .. .. .	Toxic in 6 min.
1	Distillate from acid solution .. .. .	Toxic in 9 min.
1	Distillate from alkaline solution .. .. .	Non-toxic in 1 hour.
2	Untreated effluent .. .. .	Toxic in 3 min.
2	Distillate from acid solution .. .. .	Toxic in 4 min.
2	Distillate from alkaline solution .. .. .	Toxic in 30 min.
2	Distillate from alkaline solution, re-distilled in acid solution.	Non-toxic in 1 hour.

A sample of Effluent No. 128 discharged from a gas works supplying gas to one of the towns on the banks of the Estuary had the composition shown in Table 46. The toxic constituents were volatile in acid or in neutral, but not in alkaline solution. No detailed examination of the effluent was made, but it seems probable that its toxicity was due mainly to its tar acid content, since the concentration of cyanide was small. The volume discharged was estimated at only about 1,100 gallons per day.

TABLE 46—*Gas Works Effluent, No. 128*

Parts per 100,000 :	
Total tar acids .. .. .	19
Cyanide as (CN) .. .. .	0·11
Oxygen consumed from N/8 permanganate in 4 hours at 80° F.	183
Toxicity to trout .. .. .	2 per cent. solution toxic in 24 min.

Effluent No. 14 was discharged from the gas washers of a Mond Gas Plant after removal of tar by settlement and filtration through coke. The results of



analyses of two samples of the effluent are given in Table 47. Distillation of sample No. 2 with acid gave a distillate of the same toxicity as the original sample, but a distillate from alkaline solution was not toxic in one hour. The extent to which the cyanide contributed to the toxicity is shown by the figures in Table 48, which were obtained in experiments made to determine the effect of removing the cyanide with formaldehyde. Cyanide was apparently the main toxic constituent; at low concentrations (1 per cent. or less) the effluent was non-toxic after removal of cyanide; at higher concentrations the effluent remained toxic after the removal of cyanide, owing to the toxicity of the tar acid constituents.

TABLE 47—*Effluent from Mond Gas Plant*

Sample No.	1	2
Parts per 100,000 :		
Total tar acids .. ..	16.5	32.5
Cyanide as (CN) .. ..	0.8	1.2
Oxygen consumed from N/8 permanganate in 4 hours at 80° F.	103.5	105.4
Toxic to trout in 2 per cent. solution in	8½ min.	13 min.

TABLE 48—*Effect of Cyanide Removal on Toxicity of Effluent from Mond Gas Plant*

Sample No.	Volume diluted with water to 100 volumes.	Tar acids in solution. Parts per 100,000.	(CN) in solution. Parts per 100,000.	Formaldehyde added. Ml. to 20 litres of solution.	Toxicity to Trout.
1	3	0.5	0.024	0	Toxic in 5 min.
1	3	0.5	0.024	10	„ 9 „
1	2	0.33	0.016	0	„ 8½ „
1	2	0.33	0.016	10	„ 17½ „
1	1	0.17	0.008	0	„ 36 „
1	1	0.17	0.008	5	Non-toxic.
2	2	0.65	0.024	0	Toxic in 11 min.
2	2	0.65	0.024	5	„ 15 „

Summarising the results, the main toxic constituents of the coke oven and similar effluents discharged into the Estuary are cyanides and tar acids. Cyanides are the main cause of toxicity of effluents resulting from the washing of coke oven gas with water, and tar acids are the main toxic constituent of spent still liquors. The relative importance of the two substances varies in the less important miscellaneous effluents arising from the treatment of gas by various processes. The approximate weights of tar acids and cyanides discharged into the Estuary per

day are shown in Table 49. The figures are an approximation only, since the volume of effluent discharged varies considerably from time to time.

TABLE 49—*Approximate Quantities of Tar Acids and Cyanides Discharged*

No. of Effluent.	Description.	Approximate flow Gal. per 24 hr.	Concn. in parts per 100,000.		Wt. in lb. discharged per 24 hr.	
			Tar acids.	(CN).	Tar acids.	(CN).
1a	Spent still liquor ; semi-direct process coke oven effluent.	Stated not to reach the Estuary.	200	0	—	—
10	Effluent from gas coolers ; semi-direct process coke oven effluent.	634,000	6·3	8·2	400	520
11	Effluent from tar, benzol and chemical works.	23,000	31	0	73	—
14	Effluent from gas washers of a Mond Gas Plant.	48,000	24	1	115	4
31	Effluent from gas coolers ; direct process coke oven effluent.	1,080,000	13	7·8	1,400	840
35	Effluent from water seal of gas producer.	179,000	0·02	0	—	—
59	Effluent from gas coolers ; direct process coke oven effluent.	1,080,000	12·5	4	1,350	430
128	Gas works effluent ...	1,100	19	0·11	2	—
155	Effluent from tar works ...	24,400	5·5	0	13	—
159	Spent still liquor ; semi-direct process coke oven effluent.	36,500	250	0	915	—
	Total				4,268	1,794

The cyanide and tar acids discharged are mainly in effluents from coke oven gas coolers. The weight of tar acids contributed by spent still liquors is relatively small (Table 50).

TABLE 50—*Weight of Cyanide and Tar Acids discharged in Coke Oven Effluents in 1931*

Source.	Lb. discharged per 24 hr. of	
	Tar acids.	(CN).
Effluents from coke oven gas coolers (3 effluents)	3,150	1,790
Spent still liquors (1 effluent) ... ..	915	0



## CHAPTER XIII

TOXICITY OF DIRECT POISONS DISCHARGED INTO THE ESTUARY  
AND EFFECT OF LOW CONCENTRATIONS OF DISSOLVED OXYGEN

Examination of the waters of the Estuary and of the toxic effluents discharged into them has shown that the main factors adversely affecting fish life are direct poisons, mainly tar acids and cyanides, and deoxygenation of the water<sup>(1)</sup>. Experiments were therefore carried out to determine the relative importance of these factors.

## TOXICITY OF PHENOLIC SUBSTANCES

The tar acids of coke oven effluents, as estimated by the usual analytical methods, are a complex mixture of monohydric and polyhydric phenolic substances, the exact composition of which is not known. The toxicity of tar acids was estimated from measurements of the toxicity of representative pure phenolic substances. The toxicities of equimolecular concentrations of phenol and its homologues, or of different isomers of the same substance are not exactly the same, but they are of the same order. Toxicity-concentration curves of phenol, *p*-cresol and 1.2.6.xylenol are shown in Fig. 49. All the points on any one curve represent the means of the same number of determinations, either 10 or 20. In addition to the toxicity scale, a scale showing the average times of overturning of trout is included in Fig. 49. If the relation between the time of overturning and the concentration is considered, it will be seen that equal reductions in concentration cause progressively larger increases in the time of overturning. In considering the effect of a toxic substance on a fish migrating through an estuary this relation is of great importance, for the chance of the successful passage of the fish depends largely on the length of time it can live in the polluted water.

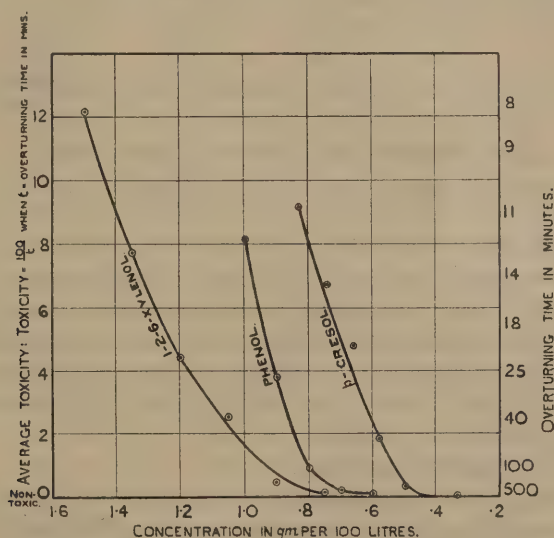


FIG. 49—Toxicity of *p*-Cresol, Phenol, and 1.2.6.Xylenol to Rainbow Trout

The toxicity of the three substances investigated is in the order *p*-cresol > phenol > 1.2.6.xylenol. Thus, the concentrations of each in which the average overturning time is 20 minutes, are :—

<i>p</i> -Cresol	..	..	0.70 gm. per 100,000 ml.	=0.000065 M
Phenol	..	..	0.94                    "	=0.0001 M
1.2.6.Xylenol	..	..	1.24                   "	=0.000102 M

There is a similar gradation in the variability of the three substances in their effect on individual fish. Thus, the average coefficients of variation of toxicity ( $100 \times \frac{\text{standard deviation}}{\text{arithmetic mean}}$ ) for all the points on each curve of Fig. 49 are : *p*-cresol, 49 per cent. ; phenol, 66 per cent. ; 1.2.6.xylenol, 99 per cent. The physiological actions of phenol and *p*-cresol, so far as they could be judged from the behaviour of fish, appeared to be similar, but they differed from the action of

1.2.6.xylenol. After a short exposure to phenol or *p*-cresol, trout became very agitated and swam rapidly round the experimental vessel, repeatedly losing and regaining their equilibrium, until they finally overturned in a helpless condition. They were sensitive to mechanical stimuli, recoiling violently when touched or if the vessel were disturbed. Similar symptoms have been recorded by many other observers<sup>(2)</sup> and there is general agreement that phenol acts as a specific poison on the nervous system of fish. In xylenol solutions the trout were much less agitated, many of them lying quietly on the bottom of the vessel; they did not move appreciably when disturbed, and they finally overturned without making any attempt to regain their balance.

TOXICITY OF POTASSIUM CYANIDE

*Toxicity-Concentration Curve*

The toxicity-concentration curve of potassium cyanide at 5° to 7° C. in aqueous solutions is shown in Fig. 50. Each point is the mean of 10 determinations. The action of cyanides on trout is more uniform than that of the phenolic poisons ;

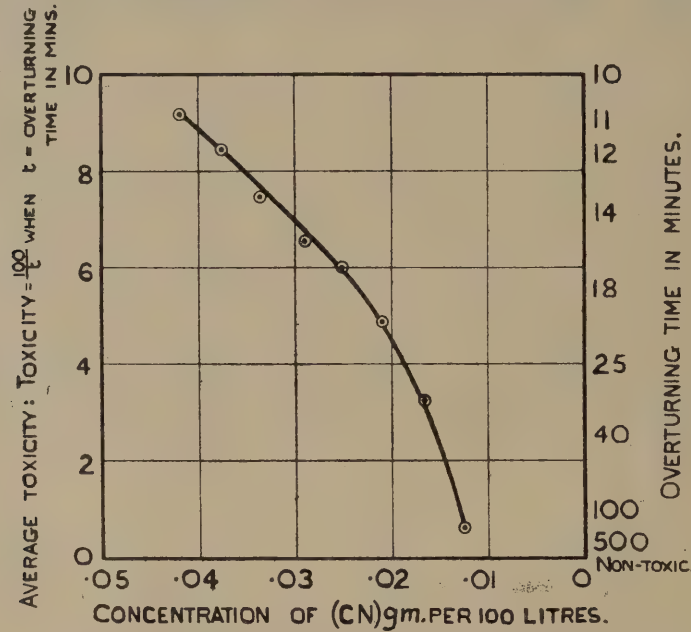


FIG. 50—*Toxicity of Potassium Cyanide to Rainbow Trout*

thus, the average coefficient of variation of all the points of the cyanide curve is only 18 per cent. as compared with 49 per cent. for *p*-cresol and 99 per cent. for 1.2.6. xylenol. In solutions of cyanide, trout usually swim quietly round the experimental vessel, and, suddenly turning over on their backs take up vertical positions, heads uppermost and with their gill covers widely distended. They rarely regain their equilibrium, the action of cyanide in this respect being markedly different from that of phenol or cresol, which cause trout to overturn many times before they are finally rendered helpless.

Of the direct poisons examined, potassium cyanide is by far the most toxic to trout. Table 51 shows the relative toxicity of cyanide and of *p*-cresol, the most toxic of the phenolic bodies investigated. The concentration of *p*-cresol toxic to trout in 11 minutes is about 20 times as great as the equally toxic concentration of cyanide, and the corresponding ratio for concentrations toxic in 100 minutes is over 40.

TABLE 51—*Toxicities of Cyanide and p-Cresol*  
Temperature 5°–7° C.

Time taken by trout to overturn  Min.	Concentration in gm. per 100,000 ml.	
	(CN)	<i>p</i> -cresol
11	0.042	0.83
20	0.0215	0.70
50	0.0145	0.59
100	0.013	0.54



*Influence of Hydrogen Ion Concentration*

The results of a series of determinations of the toxicity of solutions of potassium cyanide at different hydrogen ion concentrations are given in Table 52. In these experiments, the pH value of a measured quantity of tap water was adjusted approximately by the addition of soda or of hydrochloric acid, after which fixed quantities of potassium cyanide were added. The final pH value was then determined colorimetrically. Each toxicity value in the table is the mean of 10 determinations. Solutions of potassium cyanide equivalent to 0.03 gm. (CN) per 100,000 ml. were used in all cases. There was no significant difference between the toxicity of potassium cyanide at different hydrogen ion concentrations, the variations being no greater than the usual experimental differences.

TABLE 52—*Toxicity of Potassium Cyanide at Different Hydrogen Ion Concentrations*

Temperature 7°–8° C.

pH	Average toxicity = $\frac{100}{t}$ where $t$ = overturning time in min.	Equivalent overturning time of trout Min.
6.0	7.91	12.6
6.5	7.70	13.0
7.0	7.98	12.5
7.5	7.92	12.6
8.0	8.55	11.7
8.5	7.82	12.8
Mean	8.00	12.5

*Effect of Cyanides on Gill Colour of Trout*

During the course of a series of laboratory experiments in which trout were poisoned by various substances, it was observed that, where the trout were dying as the result of poisoning by cyanides, their gills became brighter than those of normal fish. This brightening is due to changes in the condition of the arterial blood caused by the inhibition by cyanide of the enzyme responsible for the transference of oxygen from the blood corpuscles to the body tissues. The changes brought about by cyanides and other poisons in the gill colour of rainbow trout and of sea trout smolts (netted in the Estuary and kept for some days in fresh water) were measured quantitatively by matching the gill colour of dying and normal fish against a graded colour chart. The chart consisted of a series of 8 colours ranging from bright red (Colour No. 2) to dark crimson (Colour No. 16); intermediate colours could be judged, giving a series of 15 shades in all. The colours were prepared from mixtures of scarlet, ultramarine, vermilion and brown inks (Newton's Mandarin Waterproof) diluted with distilled water<sup>(3)</sup>. Strips of Whatman's No. 1 filter paper were soaked in these solutions, excess ink being immediately removed with blotting paper; the rough side of the paper was used for comparison with the gill colours. An analysis of the colours of the chart, made with a Lovibond Tintometer modified for use with reflected light, is given in Table 53. The comparison was carried out by Mr. N. Strafford, by the courtesy of the British Dyestuffs Corporation, Ltd.

TABLE 53—*Analysis of Colours of Gill Colour Chart*

Gill Colour Scale No.	Lovibond Tintometer Units.		
	Red.	Yellow.	Blue.
2	15.8	1.5	0
4	15.3	1.5	0
6	14.2	1.9	0
8	12.8	1.9	0.3
10	11.0	2.5	1.3
12	9.5	2.5	2.6
14	8.9	2.8	3.4
16	6.0	2.8	4.0

In a typical experiment, the gill colours of sixteen fish were determined, after which they were exposed to an experimental solution. When at least half the fish had turned over on their sides they were removed, their gill colours were again observed, and they were allowed to recover in fresh water; further observations were made during the period of recovery. The results of a typical experiment are shown in Table 54 and the whole of the results obtained are summarised in Table 55. Only in the case of cyanide was there any brightening of the gill colour; a marked darkening occurred with the other types of poisons discharged into the Estuary and with oxygen deficiency.

TABLE 54—*Change in Gill Colour of Rainbow Trout in a Solution of Potassium Cyanide equivalent to 0.017 gm. (CN) per 100 Litres*

	Colour No.						Average Gill Colour No.
	5	6	7	8	9	10	
No. of fish before poisoning ...	—	—	—	2	11	3	9
No. of fish after poisoning (1 died) ...	3	6	7	—	—	—	6
No. of fish on recovery ...	—	—	3	7	4	1	8
No. of fish 1 hr. after recovery ...	—	2	4	5	3	1	8

TABLE 55—*Change in Gill Colour of Fish During Poisoning*

Increase in Gill Colour No. indicates Darkening of Colour and Vice Versa

Experimental solution.	Rainbow Trout.				Sea Trout Smolts.			
	No. of fish used.	Average Gill Colour.		Differ- ence (2)–(1).	No. of fish used.	Average Gill Colour.		Differ- ence (2)–(1).
		Before poisoning (1).	After poisoning (2).			Before poisoning (1).	After poisoning (2).	
Potassium cyanide as (CN)—								
0.017 gm. per 100 litres ..	16	9	6	–3	—	—	—	—
0.02 gm. per 100 „ ..	—	—	—	—	4	10	8	–2
1.00 gm. per 100 „ ..	13	9½	6½	–3	—	—	—	—
<i>p</i> -Cresol—								
0.7 gm. per 100 litres ..	13	8	11½	+3½	—	—	—	—
0.8 gm. per 100 „ ..	—	—	—	—	3	10	13½	+3½
1.0 gm. per 100 „ ..	13	7	10	+3	—	—	—	—
Spent still liquor containing 0.094 per cent. tar acids and no cyanide. 1 per cent. solution containing 0.94 gm. tar acids per 100 litres.	14	9	12½	+3½	—	—	—	—
Naphthalene Saturated solution diluted 1:4	8	10½	13½	+3	—	—	—	—
Fresh raw sewage. 50 percent.	25	8½	8½	0	—	—	—	—
Water deficient in dissolved oxygen.	4	10	14	+4	—	—	—	—

Since cyanides, which cause a brightening of gill colour, and tar acids, which cause a darkening, are discharged as constituents of the same industrial effluents, and are found together in the waters of the Estuary, some experiments were carried out to determine the colour effect of the mixed poisons (Table 56).



TABLE 56—Change in Gill Colour of Fish in Mixtures of Poisons  
Increase in the Gill Colour No. indicates Darkening of Gill Colour and Vice Versa

Experimental solution.	Rainbow Trout.				Sea Trout Smolts.			
	No. of fish used.	Average Gill Colour.		Difference (2)–(1).	No. of fish used.	Average Gill Colour.		Difference (2)–(1).
		Before poisoning (1).	After poisoning (2).			Before poisoning (1).	After poisoning (2).	
Potassium cyanide, 0.015gm. (CN) per 100 litres. <i>p</i> -Cresol, 0.43 gm. per 100 litres.	—	—	—	—	3	12	8½	–3½
Potassium cyanide, 0.024 gm. (CN) per 100 litres. <i>p</i> -Cresol, 0.43 gm. per 100 litres.	12	8½	7½	–1	3	11	8	–3
Effluent from coke oven gas coolers 2 per cent. solution. Solution contained :— 0.014gm. (CN) per 100 litres, 0.013 gm. tar acids per 100 litres.	14	9	7½	–1½	—	—	—	—

In the Estuary the concentration of cyanide found by analysis did not usually exceed 0.02 gm. (CN) per 100 litres, and that of tar acids 0.05 gm. per 100 litres. Even when the concentration of tar acids is twenty times that of cyanide, as in the first experiment in Table 56, the brightening due to the cyanide is well marked. In the second experiment, the concentrations of *p*-cresol and potassium cyanide were equally toxic to trout. The change in gill colour brought about by a spent still liquor, the toxicity of which is due to tar acids, is recorded in Table 55, and that brought about by an effluent from coke oven gas coolers, the main toxic constituent of which is cyanide, is recorded in Table 56. In neither of these cases did any other substance interfere with the characteristic gill colour change of the main toxic constituent. The data for sea trout smolts are not so complete as those for rainbow trout owing to the difficulty of keeping the smolts, but since the reaction of the two species to the substances in which they were tested is similar, it is reasonable to suppose that it would also be similar for other substances.

TOXICITY OF MIXTURES OF POISONS<sup>(4)</sup>

In considering the toxicity of the waters of the Estuary, which contain appreciable quantities of tar acids and cyanides, together with sub-lethal concentrations of other toxic substances, it is of importance to determine the relation between the toxicity of a mixture of poisons and that of its separate constituents. The toxicity of different pairs of substances when mixed was compared with the sum of the toxicities of the two substances acting separately. The concentration of each component in which trout overturned in approximately the same length of time was first found by trial. Each of these concentrations was taken as 100, and the toxicity of solutions containing various fractions of one of them (*x* per cent.) mixed with the complementary fraction, (100 – *x*) per cent., of the other was determined.

Potassium Cyanide and *p*-Cresol

From the curves in Fig. 51, showing the toxicities of solutions of potassium cyanide, of *p*-cresol, and of mixtures of these two substances, it appears that the

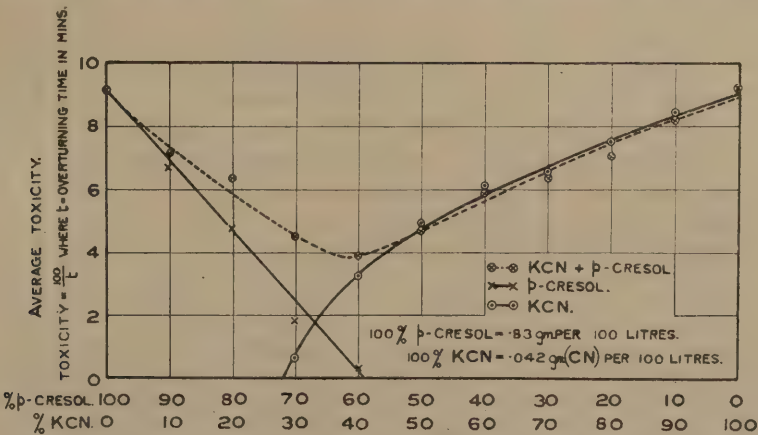


FIG. 51—Toxicity of Mixtures of Potassium Cyanide and *p*-Cresol to Rainbow Trout

toxicity of lethal concentrations of *p*-cresol is increased by adding sub-lethal concentrations of potassium cyanide but that the toxicity of lethal concentrations of potassium cyanide is unaffected by the addition of sub-lethal concentrations of *p*-cresol.

### *p*-Cresol and Phenol

The curves in Fig. 52 indicate that, as regards toxicity, *p*-cresol and phenol are interchangeable; it is possible that they have a similar action on fish. For

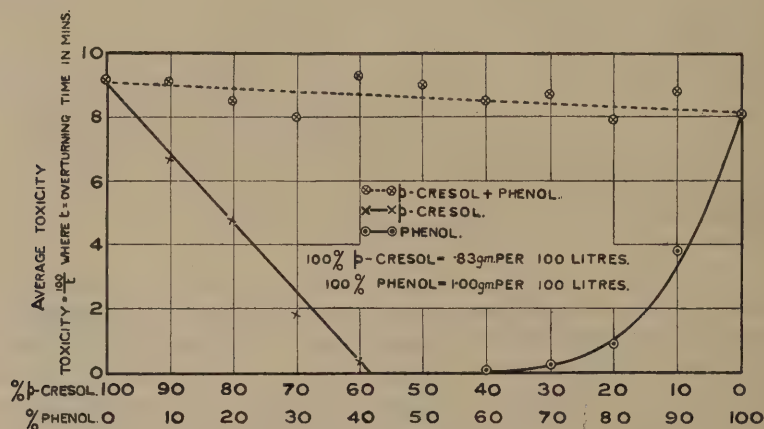


FIG. 52—Toxicity of Mixtures of *p*-Cresol and Phenol to Rainbow Trout

example, a solution of 0.83 gm. of *p*-cresol in 100 litres has a toxicity of about 9, and a solution of 1.00 gm. of phenol in 100 litres has a toxicity of about 8. A mixture of the two substances, each in a concentration of one-half these amounts, that is, containing 0.415 gm. of *p*-cresol and 0.50 gm. of phenol in 100 litres, has an intermediate toxicity of 8.5 although separate solutions of 0.415 gm. of *p*-cresol or 0.50 gm. of phenol per 100 litres are non-toxic.

### *p*-Cresol and 1.2.6.Xylenol

It might have been expected that curves representing the toxicities of solutions of *p*-cresol, 1.2.6.xylenol, and mixtures of these two substances would have been similar in type to the curves in Fig. 52 for *p*-cresol and phenol. Experiments with *p*-cresol and 1.2.6.xylenol, however, gave the curves shown in Fig. 53 which more nearly resemble those in Fig. 51 for potassium cyanide and *p*-cresol. For example, the addition of sub-lethal concentrations of *p*-cresol to toxic solutions of xylenol had no appreciable effect on the toxicity. Sub-lethal concentrations of xylenol, however, increased the toxicity of solutions of *p*-cresol.

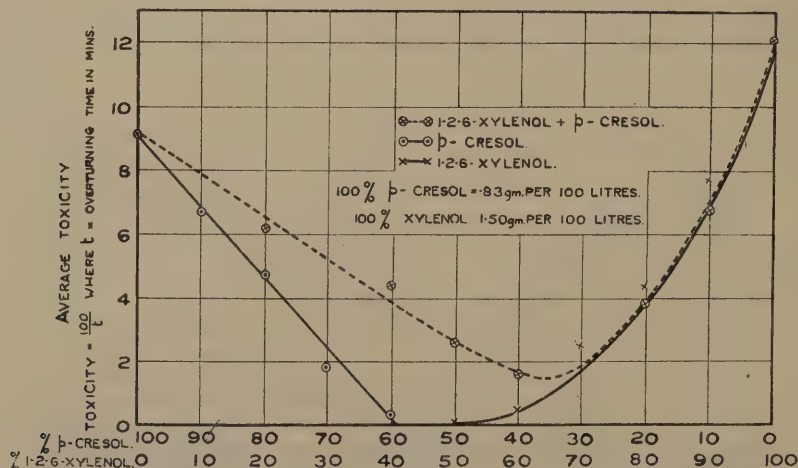


FIG. 53—Toxicity of Mixtures of *p*-Cresol and 1.2.6.Xylenol to Rainbow Trout



### 1.2.6.Xylenol and 1.3.5.Xylenol

Preliminary experiments on the toxicity of 1.2.6.xylenol and 1.3.5.xylenol and mixtures of these two substances gave the following results :

	Toxicity
1.5 gm. 1.2.6.xylenol in 100 litres .. ..	9.15
5.0 gm. 1.3.5.xylenol „ „ .. ..	9.54
0.75 gm. 1.2.6.xylenol „ „ .. ..	0.07
2.50 gm. 1.3.5.xylenol „ „ .. ..	3.14
0.75 gm. 1.2.6.xylenol } in 100 litres ..	6.12
plus 2.50 gm. 1.3.5.xylenol }	

These results indicate that mixtures of 1.2.6. and 1.3.5.xylenols would give a toxicity curve of a type intermediate between those for mixtures of *p*-cresol and phenol and mixtures of *p*-cresol and 1.2.6.xylenol.

### Cyanides and Tar Acids in the Estuary

In the Estuary the main toxic substances are tar acids and cyanides. The toxicity of the cyanides will not be appreciably increased by that of tar acids, and as tar acids are shown later to be present only in sub-lethal concentrations, whilst cyanide may be present in toxic concentrations, the cyanide is clearly of greater importance.

From the experiments described it appears that the discharge into a polluted water of a sub-lethal concentration of a toxic substance may have one of the following effects. If the new poison and the poisons already present have a different physiological action the addition may either cause no change in toxicity (e.g. sub-lethal concentrations of *p*-cresol added to potassium cyanide or very small amounts of *p*-cresol added to 1.2.6.xylenol), or the toxicity of the polluted water may be slightly increased (e.g. sub-lethal concentrations of potassium cyanide added to toxic concentrations of *p*-cresol, or of 1.2.6.xylenol, to toxic concentrations of *p*-cresol). If the new poison is the same as, or is interchangeable with, one already present, large increases in toxicity may occur (e.g. sub-lethal concentrations of *p*-cresol added to phenol, or vice versa).

As examples applicable to the conditions in the Tees Estuary, the addition of *p*-cresol in a concentration of 0.4 gm. per 100 litres to water containing coke oven effluent, the toxicity of which was due mainly to cyanide, had no effect, but a similar addition of *p*-cresol to an effluent whose toxicity was due primarily to tar acids considerably increased its toxicity.

### EFFECT OF LOW CONCENTRATIONS OF DISSOLVED OXYGEN

Many observers have determined the dissolved oxygen concentration below which various species of fish are asphyxiated. Several methods of experiment have been used, the majority of them consisting essentially in maintaining fish in water in which the oxygen content is gradually reduced, the concentration being determined when the fish overturn. By these methods the lower limit of dissolved oxygen concentration below which fish are unable to survive for short periods is found. A method of this kind was used during the survey of the river Tees to determine the asphyxial point of rainbow trout.

Tap water was boiled for about 3 hours in an open vessel and then cooled out of contact with air. If necessary, aerated tap water was afterwards added to raise the concentration of dissolved oxygen to the desired value. As the result of boiling, carbon dioxide was expelled from the tap water and the pH value usually rose to above 9.0. Carbon dioxide was therefore bubbled through the water until the pH value dropped to approximately 7.0. The experimental vessel consisted of a 20-litre glass jar with a horizontal wooden disc which fitted firmly just below the surface of the liquid. This disc prevented fish rising to the surface and minimised the absorption of oxygen from the atmosphere. Twelve litres of water were used in each experiment. Four trout, each weighing 4 to 5 gm., were introduced and the time was observed when two of them overturned. The concentration of dissolved oxygen was determined at the beginning and end of each experiment on samples of water withdrawn through a rubber valve in the centre of the wooden disc. During the short time the fish remained in the water, the oxygen content did not alter appreciably. The pH value of the water used ranged from 6.8 to

7.4. The results in Table 57 show that the minimum amount of dissolved oxygen (expressed as a percentage of the saturation value) which is necessary to support trout increases with rise of temperature. Thus, a concentration of 14 per cent. of the saturation value was not lethal in 74 minutes at a temperature of 9° to 10° C.,

TABLE 57—*Effect on Trout of Low Concentrations of Dissolved Oxygen*

Temperature °C.	Dissolved oxygen con- centration. Per cent. of saturation.	Duration of experiment. Min.	Condition of two trout out of four.
9-10	18	35	Unharmcd
	14	74	"
	12	5	Overturncd
10-11	21	30	Unharmcd
	14	5	Overturncd
12-13	39	100	Unharmcd
	19	50	"
	17	35	"
16-17	49	157	Unharmcd
	26	120	"
	21	110	"
17-18	18	30	Overturncd
	7	5	"

but at 17° to 18° C. trout overturncd in 30 minutes in a concentration of 18 per cent. The results are in general agrccmcnt with those found for brown trout by Gardner and Leatham<sup>(5)</sup>.

Results of short period experiments of this kind are not sufficient to define the minimum conditions of dissolved oxygen in which fish will live normally over long periods. Usually if fish are to maintain themselves in a given habitat, the conditions of oxygenation must be favourable to them during the whole of their life history, from the egg to the adult and spawning stage. Borderline conditions not sufficiently adverse to cause their death may, indirectly, result in their disappearance, either by intensifying the effects of disease or by causing them to migrate to a more favourable environment. These considerations apply to the fish which would normally inhabit the Estuary of the Tees. With salmon and sea trout smolts, which pass fairly rapidly through the Estuary, it is sufficient to determine their minimum oxygen requirements during migration.

Determination of the oxygen requirement of a fish over a period of several days presents difficulties. It is necessary to maintain a continuous supply of partially deoxygenated water, which involves the use of large-scale de-aerating apparatus. An investigation of this kind was not attempted during the survey. In the summer of 1932, however, the dissolved oxygen content of the laboratory tap water supply was found to be abnormally low, and the effect of this water on rainbow trout was determined<sup>(6)</sup>. A continuous stream of tap water was circulated through a carboy containing rainbow trout, the water entering by a tube dipping to the bottom of the vessel and leaving by a tube cut off at the level of the cork. The carboy thus remained completely full of water. The experiment began on 2nd August and ended on 5th September. The concentration of dissolved oxygen varied from 37 to 58 per cent. of the saturation value, with a mean of 48 per cent., and the temperature varied from 14.5 to 17° C., with a mean of 15.5° C. The fish were fed daily and remained throughout the experiment in a healthy and well-nourished condition. In a second experiment rainbow trout were unharmcd by exposure for 68 hours to water at a temperature of 4½° C., in which the dissolved oxygen concentration was maintained at only 25 per cent. of the saturation value.

The minimum dissolved oxygen concentration necessary for trout over periods of some days probably lies, therefore, between the limits of approximately 20 per cent. of the saturation value, which is fatal after short periods, and 37 to 48 per cent. in which they lived comfortably. No similar determinations have been



carried out with salmon or sea trout smolts, but it has been shown that their susceptibility to direct poisons is of the same order as that of rainbow trout or brown trout. In some instances smolts were left overnight in non-toxic solutions. In 9 instances the initial oxygen content ranged from 67 to 77 per cent. of the saturation value and the final content from 19 to 70 per cent. and the smolts were removed unharmed after 13 to 14 hours' exposure; in one instance, when the oxygen concentration fell to 13 per cent., the smolt overturned but recovered after it had been transferred to aerated water.

Summarising the work discussed in this Chapter and in Chapters XI and XII, the following are the main conclusions:

1. Of the toxic substances discharged into the Tees Estuary, cyanides and tar acids are the most important.
2. The weight of tar acids discharged at the time of the survey was approximately  $2\frac{1}{2}$  times the weight of cyanides but the toxicity of cyanides is very much higher than that of tar acids, so that cyanides are by far the most important substances contributing to the toxicity of the Estuary waters.
3. Trout can live for long periods in water containing dissolved oxygen as low as 37 to 50 per cent. of the saturation value and probably in even lower concentrations.
4. The toxicities of cyanide and the phenolic substance *p*-cresol are greatly increased as the concentration of dissolved oxygen is lowered.

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## CHAPTER XIV

## MIGRATION OF SMOLTS

## SMOLT MIGRATIONS OF 1930 AND 1931

The observations made during the migration in 1930 were largely of a preliminary nature, for little or no exact information was available on the usual period of migration and on the intensity and locality of the mortality to be expected. Dead smolts were picked up on the Estuary banks from 28th April to 12th June but it was reported that smolts had been seen in the Estuary in the middle of April. This information was probably correct since the first smolts found were so decomposed that they must have been dead for more than a week. The first large batch of dead smolts was picked up above Stockton, near the upper limit of salt water in the Estuary, and during the remainder of the migration period both banks of this section of the Estuary were searched on most days for dead fish. Above Stockton the Estuary runs through open country and there are towpaths on both sides, so that it is easy to examine the banks at low water. Below Stockton, however, the industrial part of the Estuary begins and the banks consist largely of wharves, often hidden by ships moored alongside them. It was not therefore possible to search this part of the Estuary as thoroughly as the reaches above Stockton. This probably accounts for the larger number of dead smolts found above Stockton than below. Most of the smolts were picked up during periods of high springs. At the time it was thought that smolt mortality above Stockton occurred mainly during springs and observations on the condition of the Estuary water were made only during such periods.

About three hours before high water of high springs in May, 1930, salmon and sea trout smolts began to appear, usually near Stockton, swimming slowly close to the surface of the water. As the tide rose, the enfeebled fish were carried upstream, until by high water they were generally between Bassleton Wood and Thornaby Wood, some  $2\frac{1}{2}$  miles further up-stream. During this movement, they were usually followed by a flock of gulls, which fed greedily on them; large numbers were also killed and taken away by people on the Estuary banks. In the early part of May, when the water temperature was comparatively low, the symptoms shown by the dying smolts were less intense than later in May and in June, when the temperature was higher. In early May the smolts swam feebly near the surface of the water, especially near the banks, where many of them were left stranded as the tide fell. In the later part of the period of migration, they appeared quite suddenly at the surface, swam rapidly round in circles, often swimming on their sides, and after a few minutes disappeared equally suddenly. Sometimes a fish would swim violently in an almost vertical position, with its head out of the water.

During the period of migration in 1930, 2,426 dead salmon and sea trout smolts were picked up on the Estuary banks; of these less than 200 were found below Stockton. They were examined by Mr. F. T. K. Pentelow in order to ascertain whether their post-mortem appearance indicated the cause of death. The macroscopic examination of the main organs, however, gave no such information. All the smolts were measured and scales were taken from some for determinations of age.

At high water springs, series of samples of Estuary water were taken on ten days in the reaches of the Estuary above Stockton, where smolts were seen dying. The salinity of the water in the mortality stretch ranged from less than 1 gm. per 1,000 gm. at the upper end to 16.7 gm. per 1,000 gm. at the lower; the average was approximately 10 gm. per 1,000 gm. The concentrations of tar acids found ranged between 0.005 and 0.02 parts per 100,000, except for one value of 0.06 parts per 100,000; none of these concentrations is sufficiently high to be toxic to fish. The method later used for cyanide determinations had not then been fully standardised, and the values it gave were probably too low; they ranged



from 0 to 0.02 parts (CN) per 100,000. A concentration of 0.02 parts (CN) per 100,000 is sufficient to cause trout to overturn in less than 15 minutes. The water temperature during the migration was at first about 10° C., and rose gradually during May to 16° C. At the same time there was a decrease in the concentration of dissolved oxygen, in terms of percentage saturation. On 29th April the oxygen content of the water in which smolts were dying ranged from 70 to 75 per cent. of saturation, and up to 26th May no value under 43 per cent. was recorded. From 27th to 30th May a sharp rise in temperature and fall in dissolved oxygen values occurred; the oxygen values on 30th May were only 20 to 58 per cent. of the saturation value. At the end of the migration period the deficiency of dissolved oxygen was probably great enough to account for the death of smolts and must certainly have increased the toxicity of any directly poisonous substances present. During the first part of the migration period, however, it is certain that deficiency in dissolved oxygen was not the cause of mortality.

The main problems on which attention was concentrated in 1931 were the causes of the smolt mortality, the distribution of toxic substances in the Estuary under different conditions of fresh water flow and tidal range, and the movements of smolts in the Estuary during their passage to the sea.

### CAUSES OF SMOLT MORTALITY

#### *Toxicity of Estuary Water*

Systematic sampling of Estuary water was begun on 15th April, 1931, before the migration had started, and was continued until 5th June, 1931, when the migration had ceased. From observations in 1930 of dying fish and the position of dead smolts, it appeared that the smolt mortality took place mainly, if not entirely, at about the time of high water. In 1931, therefore, samples were systematically collected each day from Cleveland Shipyard to above Stockton at about the time of the high water which occurred between 6 a.m. and 6 p.m. <sup>(1)</sup>. They were taken from the motor launch which left Cleveland Shipyard one hour before high water and travelled as rapidly as possible up the Estuary. In this way the samples were collected from day to day under approximately comparable tidal conditions. When dying smolts were observed, additional samples were taken in the area of mortality and in a stretch of the Estuary seawards of it. On days when no smolts were seen it was not possible to ascertain whether there was a toxic stretch without collecting samples throughout the whole length of the Estuary; a toxic stretch may, therefore, have been present on these occasions outside the area examined.

During 51 days of the migration period 570 samples were taken for determinations of salinity, temperature, pH, dissolved oxygen concentration, and, usually, of cyanide and tar acids. In addition, a series of samples was taken for the determination of the toxicity of the water to fish and the effect of the removal of cyanide on the toxicity (Appendix II). For the experiments on toxicity, two demijohns, each containing about 20 litres of water, were drawn daily from each of about nine positions in the Estuary. The water from one of each pair was poured into a wide mouthed earthenware jar to which 1.5 ml. of 38 per cent. formaldehyde had been added and, to ensure intimate mixing, was afterwards poured into another vessel and finally back into the original jar; the duplicate sample which served as a control was not mixed with formaldehyde but was otherwise similarly treated. It had been found (Appendix II) that treatment with formaldehyde destroyed cyanides without affecting the concentration of tar acids; the addition of formaldehyde and the subsequent mixing did not cause any appreciable alteration in the concentration of dissolved oxygen. It was at first intended to determine the toxicity of these samples to smolts netted in the Estuary, but it was found that a smolt if left overnight in only 20 litres of water so reduced the oxygen content that the fish was in danger of dying from oxygen deficiency. Rainbow trout were, therefore, used as the test fish, one trout being tested in each sample. They were usually watched for some hours after being placed in the water and were removed if they overturned. Samples which did not affect trout after 10 to 20 hours were regarded as non-toxic. Dissolved oxygen

concentrations and temperatures were taken at the beginning and end of each experiment. There was never any appreciable difference between the final oxygen contents of the untreated samples and those to which formaldehyde had been added. The numbers of toxic and non-toxic samples, and the effect of the addition of formaldehyde are shown in Table 58. Of 283 samples examined, 138 or 49 per cent. were toxic ; of these, the toxicity of 130 (94 per cent.) was destroyed by the removal of cyanide with formaldehyde. The deaths of 5 fish, in solutions which were originally innocuous but were rendered toxic by the addition of formaldehyde, were probably due to the effects of salinity or to an overdose of formaldehyde ; the quantity of formaldehyde added (equivalent to 3 gm. per 100 litres) was only just below the minimum concentration toxic to trout. Some of the deaths of 8 fish in samples which were toxic both with and without addition of formaldehyde may have been due to similar causes.

TABLE 58—*Toxicity of Estuary Water before and after Removal of Cyanide*

	No. of samples
Non-toxic untreated ; toxic with formaldehyde	5
" " " non-toxic with formaldehyde	140
Toxic untreated ; non-toxic with formaldehyde	130
" " " toxic with formaldehyde	8

In the great majority, if not all, of the toxic samples examined the toxicity was due to the presence of cyanides. This is borne out by a comparison of the percentage of toxic samples in groups containing various ranges of cyanide concentration as found by analysis (Table 59). A second series of values, obtained in the same way during surveys of the Estuary at low water after the period of the smolt migration, is included for comparison.

TABLE 59—*Toxicity of Estuary Water and Concentration of Cyanide*

Concentration of cyanide  Gm. (CN) per 100,000 ml.	1. Samples taken during smolt migration of 1931.		2. Samples taken in summer of 1931.	
	No. of samples.	No. of toxic samples.	No. of samples.	No. of toxic samples.
		Per cent.		Per cent.
0	84	13	249	2
0.002	37	19	78	23
0.003-0.004	45	62	19	63
0.005-0.006	32	84	10	90
0.007-0.008	15	93	7	100
0.009-0.010	12	100	4	100
>0.010	23	100	6	100

The accuracy of the methods of determination of cyanides is discussed in Appendix I where it is shown that the concentration of (CN) given by analysis is in general considerably lower than the amount actually present, especially with small concentrations. The values in Table 59 therefore, while showing the relative concentrations of cyanide in the groups of samples, are lower than the true values.

The concentrations of tar acids in the samples, as found by analysis were generally of the order of 0.01—0.03 parts per 100,000 ; the maximum observed value was 0.05. These concentrations are much lower than the minimum toxic to trout.



It has been mentioned (Chapter XIII) that trout have been kept for 34 days in water containing dissolved oxygen to the extent of 37 to 58 per cent. of the saturation value and that other short period experiments indicated that the minimum concentration necessary for trout over periods of some days is considerably lower. The concentrations in the Estuary, 40 to 70 per cent. of the saturation value in samples of water in which smolts were dying, were probably never sufficiently low to be responsible for the death of the fish. This is borne out by the fact that the majority of samples of Estuary water in which the cyanide had been removed by formaldehyde were harmless to trout over long periods, although the dissolved oxygen concentration was not appreciably altered by the treatment of the sample. Occasional samples of Estuary water were aerated continuously over the period in which trout were exposed to them. In some cases the oxygen concentration rose nearly to the saturation value but all samples which contained cyanide remained toxic to trout.

#### *Gill Colour of Smolts Found Dying in the Estuary*

The colour of the gills of salmon and sea trout smolts or of rainbow trout becomes brighter when these fish are being poisoned by cyanides, but becomes darker during poisoning with any other toxic substance found in the Estuary (Chapter XIII). During the migration in 1931 large numbers of smolts were picked up in a dying condition in the Estuary and their gill colours were compared with the colours of a standard chart. Since a dead fish has a very dark gill colour, whatever the cause of death, only those fish were examined which were obviously alive. Some of the smolts were brought to the laboratory and were allowed to recover in a tank of fresh water, so as to obtain records of normal gill colour for comparison. The average recorded gill colours of dying and normal smolts are given in Table 60. The gill colours of the dying smolts were considerably brighter than those of normal fish and the difference was of the same order as that found in experiments with cyanide in the laboratory. The records thus confirm the chemical observations in attributing the death of smolts in the Estuary to poisoning by cyanides.

TABLE 60—*Gill Colours of Normal Smolts and of Smolts Found Dying in the Estuary*

	Salmon Smolts.		Sea Trout Smolts.	
	Dying.	Normal.	Dying.	Normal.
No. of fish from which records were taken .. ..	66	40	131	76
Average gill colour .. ..	8.5	12.5	7.1	11.7

#### DISTRIBUTION OF TOXIC SUBSTANCES IN THE ESTUARY

The determination of the toxicity of samples of water taken from the Estuary during the smolt migration showed the presence of a stretch of poisonous water, the position of which, at a given state of the tide, varied from day to day. The positions occupied by the toxic stretch at high water are shown in Fig. 54; the toxicity values from which the graph is constructed refer to samples taken usually from the surface and in no case from a depth greater than 1 fathom. The upstream limit of the toxic stretch is fairly well defined in most cases, but the position of the seaward limit is much less definite, since fewer samples were taken in this region. The upper limit of the area of mortality moved from day to day in a periodic manner; there was a well marked maximum up-stream position on 2nd to 5th May, with less well defined maxima on 20th to 22nd and on 30th May, while marked down-stream limits occurred on 11th and 24th to 26th May. The volumes of the industrial effluents responsible for the toxicity did not vary appreciably from day to day, and the factors most likely to cause changes in the distribution of toxic substances were the volume of fresh water and the tidal

range. The variations of these factors have been plotted in Fig. 54; the volume of the fresh water flow on each day is obtained from the mean of three readings of the gauge at Croft on the previous day. There is no doubt that large floods from the upper river may dilute the Estuary waters to an extent sufficient to cause the disappearance of the toxic stretch, although from 30th May to 3rd June, when the upper river was heavily flooded, stretches of the Estuary were found to be toxic. The position of the toxic stretch varies mainly with the tidal range, moving up-stream above Stockton during high springs and less far up river during neaps. This is confirmed by a consideration of the positions in which dead smolts were found during the years 1929 to 1931.

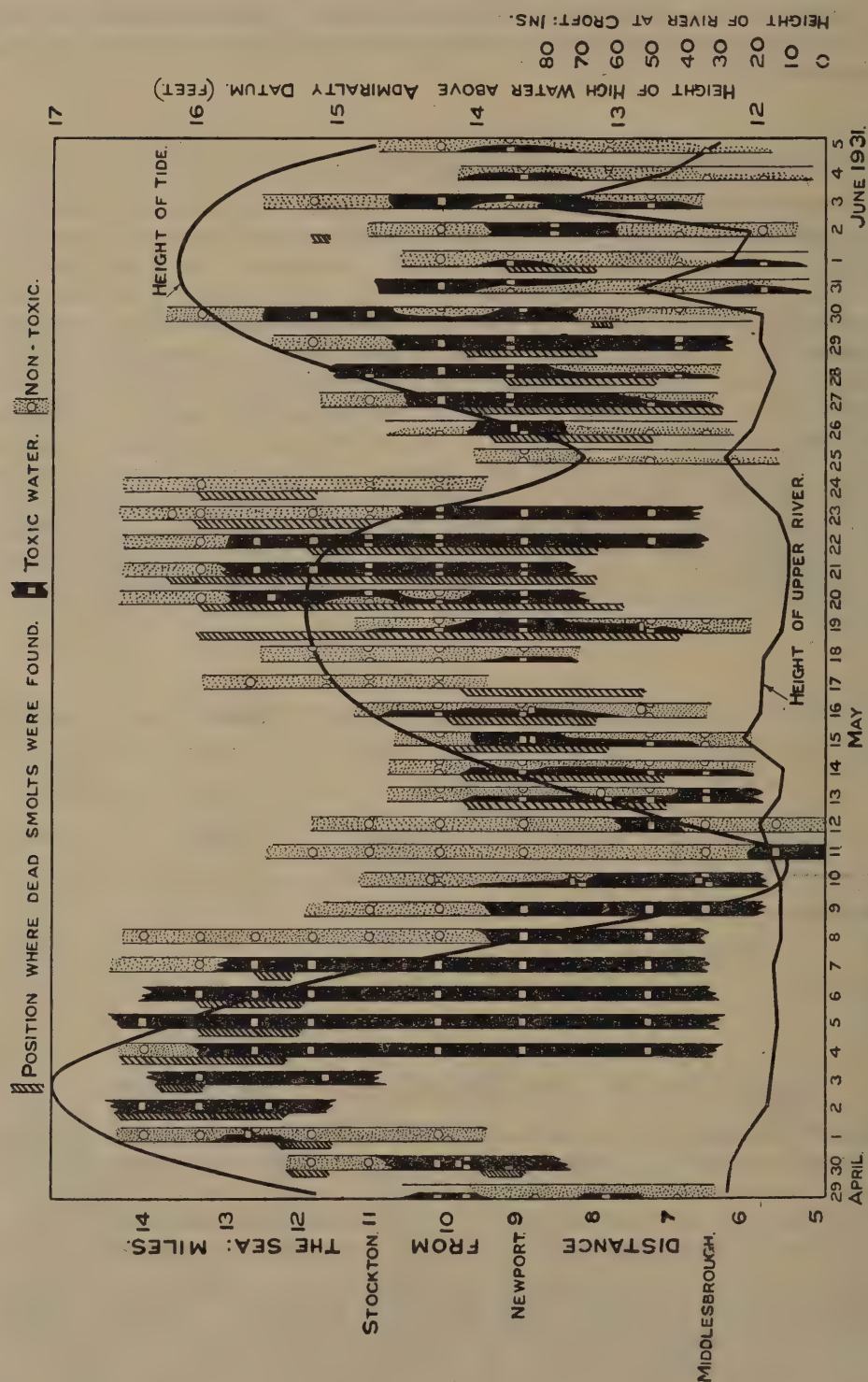


FIG. 54—Position of Toxic Area in the Tees Estuary at High Water during the Smolt Migration of 1931

The majority of smolts were killed at about the time of high water, and in dying they usually congregated near the banks where they were left stranded as the tide ebbed. They were usually found at low water in reaches of the Estuary which had been occupied by toxic water at high water (Fig. 54). The exceptions are probably explained by the fact that the position of the toxic stretch was



determined at only one high water (occurring in daylight) of the two daily tides, and dead smolts were collected only during the low water period in daylight. It is probable that roughly half of the dead smolts found were killed during the unobserved high water period. Since the tidal range of the two daily tides is in general different, the position of the toxic stretch during the unobserved high water period would be correspondingly different from that during the daylight high water. The only records available for 1929 show that smolts were killed above Stockton on 8th and 9th May at high water during springs, and again on 15th and 16th May at Cleveland Shipyard (over 7 miles further seaward) during neaps. In 1930, the majority of smolts brought in were found dead during springs on the banks above Stockton, the only part of the Estuary where the banks were thoroughly searched. From 17th to 20th May, however, during a period of neaps, they were found dead between Newport and Cleveland Shipyard.

At high springs polluted water will be forced further upstream than at neaps ; the average distance travelled by the surface layers during the flood is about three times as far during springs as during neaps<sup>(2)</sup>. It appears from Fig. 54, however, that there may be some other factor causing a localisation of the toxic material during neaps. It was thought that there might be a tendency for the toxic effluents responsible for the smolt mortality to remain after their discharge in the bottom layers of the Estuary waters, especially during neaps when less vertical mixing occurs than during springs. A series of samples was, therefore, taken at different depths throughout the Estuary, and their toxicity to trout determined. The results are summarised in Table 61. The relative frequencies of occurrence of toxic water at different depths were : at surface, 20 cases ; at 1 fathom, 14 cases ; at bottom, 8 cases. It is evident that the heavy layer of salt water which enters the Estuary from the mouth and moves up-stream along the bottom remains relatively less polluted than the water moving seaward above it, and gives a safer passage to migrating fish than the surface waters. It should be pointed out, however, that all the samples referred to in Table 61 were taken seaward of Stockton, where the extent of vertical mixing of the Estuary water is less than in the higher undredged shallow reaches in which almost complete vertical mixing occurs on every large flood tide. A homogeneous barrage of toxic water, which must be traversed by smolts migrating to the sea during a high water period, may thus be formed above Stockton.

TABLE 61—*Relative Toxicity of Water at Different Depths in the Tees Estuary*

Depth of Sample.				T = Toxic ; N = Non-toxic.					
Surface	..	..	..	T	T	T	T	N	N
1 fathom	..	..	..	N	T	T	N	N	T
Bottom	..	..	..	N	N	T	T	T	N
No. of cases	..	..	..	10	5	4	1	1	2
									3
									21

The effluents which contain cyanide are all discharged from the south bank of the Estuary, and the toxicity near the south bank, even at some distance from the points of discharge, is considerably higher than near the north bank. Thus, of 39 occasions during the smolt migration when samples were taken on both sides of the river and one or both proved to be toxic, the differences between the toxicity on the two sides was as follows :—

Toxic near S. bank and non-toxic near N. bank	..	..	13 cases
More toxic near S. bank than near N. bank	..	..	17 „
Equally toxic near both banks	..	..	6 „
More toxic near N. bank than near S. bank	..	..	3 „
Toxic near N. bank and non-toxic near S. bank	..	..	0 „

It is probable that lateral mixing is greater during springs than during neaps, when there is less movement of the Estuary water.

The numbers of dead smolts found on the Estuary banks are shown graphically in Fig. 55, together with the height of the upper river and the tidal range. It will be remembered that in 1930 almost all the smolts picked up were found on the Estuary banks above Stockton and their numbers were closely related to the tidal range, the maximum mortality occurring at springs and little or none at neaps. During that migration dying smolts were never seen in large numbers below Stockton. The dead were collected partly by the Middlesbrough staff, assisted, in the reaches

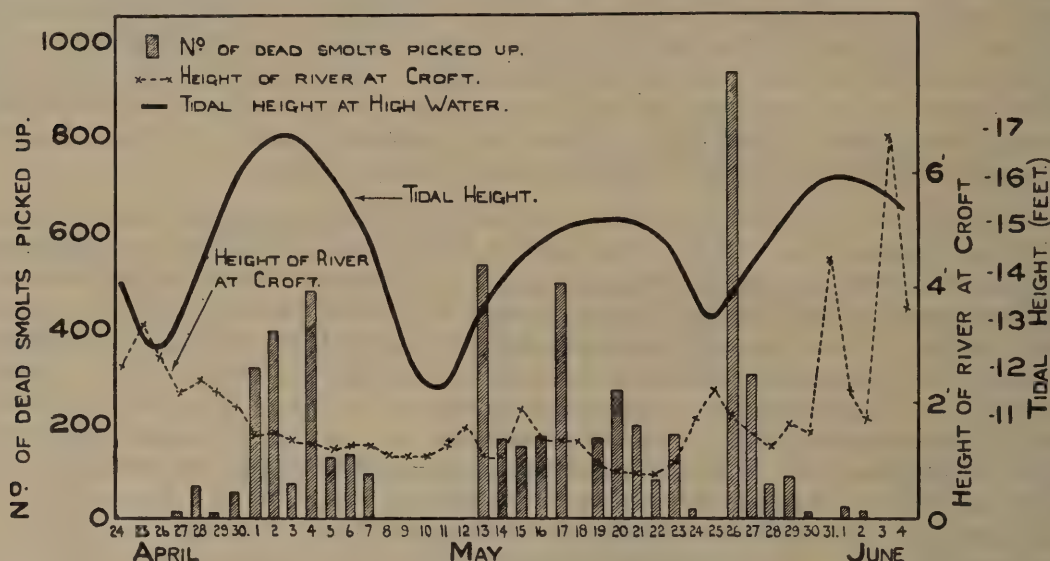


FIG. 55—Number of Dead Smolts found in the Tees Estuary during the Smolt Migration of 1931

above Stockton, by a hired boatman. In 1931 the same arrangements were made at first for collecting dead smolts as in 1930 but after 13th May, 1931 a more intensive search throughout the whole length of the Estuary was organised. It will be seen (Fig. 55) that from 13th May the total numbers of dead smolts brought in no longer bore any relation to the tidal range; the numbers found above Stockton, however, continued to do so. During springs the dead smolts were again found above Stockton but during neaps they were brought in also from the lower reaches of the Estuary, their positions corresponding fairly closely with the up-stream limit of the toxic stretch of the Estuary at high water. The height of the river at Croft was not appreciably different during the 1930 and 1931 migrations except that in 1931 it rose abruptly on 30th May; the migration was by that time, however, almost ended. The extent to which the number of smolts killed depends on the range of tide is thus still unsettled. It has been shown that the toxic stretch of the Estuary is situated further seawards during neaps than during springs, and that it tends to become shorter or in some cases to disappear entirely in the surface layers at neaps. It is possible that there is a comparatively non-toxic stretch of water near the north bank of the Estuary, and that some smolts may thus be able to pass safely to sea.

#### MOVEMENTS OF MIGRATING SMOLTS

During the smolt migration period of 1931 it was decided to fish for smolts in the reach of the Estuary above Stockton, where the main mortality was thought to have occurred in 1930, in order to determine whether there was any periodicity in the movements of smolts past that point.

Fishing was carried out at Thornaby Wood, about  $2\frac{1}{4}$  miles above Stockton Ferry, with a boom net, 12 ft. wide at the mouth by 6 ft. deep; the upper, wooden boom floated at the surface and the net was kept open by the weight of the lower iron boom. The net was worked from a rowing-boat moored near the south bank in order to fish in the fastest part of the current. The water at this point is always fresh at low water and the salinity rises to an average value of 10 gm. per 1,000 gm. at high water. It was only possible to fish during the period from about  $2\frac{1}{2}$  hours before to  $2\frac{1}{2}$  hours after high water, as the current at other states of the tide was too strong and the water too shallow to allow of the net being used. Fishing was carried out on both day and night tides, except on Saturday night and Sunday.



The fish caught included salmon (*Salmo salar*) and sea trout (*S. trutta*) smolts, brown trout (*S. trutta*), flounders (*Pleuronectes flesus*), three-spined sticklebacks (*Gasterosteus aculeatus*), chub (*Leuciscus cephalus*), eels (*Anguilla anguilla*), sparring (*Osmerus eperlanus*), minnows (*Phoxinus phoxinus*) and lamperns (*Lampetra fluviatilis*). A record of the numbers caught of the types most frequently netted is given in Table 62.

TABLE 62—Records of Smolt Netting at Thornaby Wood, 21st April—5th June, 1931

Date	No. of tides fished	Eels	Flounders	Sticklebacks	Salmon smolts	Sea Trout smolts	No. of hours darkness fished 9 p.m.—4 a.m. G.M.T.	No. of smolts caught per hour of darkness fished	Average height of river at Croft for preceding day In.	Maximum height of tide Feet	Visibility of Secchi disc at high water of the daylight tide Depth In.
April 21	1	0	2	1	0	0	0	0	28	15.3	—
" 22	1	0	0	0	0	0	0	0	27	14.6	—
" 23	1	0	0	0	1	0	0	0	26	14.4	—
" 24	1	0	0	0	0	0	0	0	28	13.9	—
" 25	1	1	0	1	0	0	0	0	31	13.0	—
" 27	1	0	0	0	0	1	0	0	34	13.1	23
" 28	2	2	9	3	0	5	4	$\frac{1}{2}$	26	14.1	27
" 29	2	2	23	3	3	2	4	$\frac{1}{4}$	28	15.1	27
" 30	2	18	48	7	1	5	4	$\frac{1}{4}$	27	16.0	—
May 1	2	34	72	28	20	27	3	9	23	16.6	19
" 2	1	24	8	2	13	22	2	13	17	16.9	16
" 4	2	9	23	7	5	8	1	12	16	16.5	16
" 5	2	12	20	8	5	11	$\frac{1}{2}$	2	15	16.1	18
" 6	2	6	8	1	12	4	0	0	14	15.6	24
" 7	2	7	11	2	7	7	1	2	15	14.7	—
" 8	2	7	5	0	10	5	2	4	15	13.5	39
" 9	1	6	3	0	1	0	0	0	13	12.3	36
" 11	1	0	0	0	0	0	0	0	13	11.8	36
" 12	2	4	5	0	6	4	4	3	15	12.6	42
" 13	2	1	1	1	3	6	4	2	19	13.2	35
" 14	2	3	8	6	12	3	4	0	13	13.9	30
" 15	2	4	15	3	32	16	$3\frac{1}{2}$	0	12	14.4	28
" 16	1	5	28	1	10	24	3	11	23	14.8	—
" 18	2	1	8	2	46	11	1	9	18	15.1	24
" 19	2	11	9	13	29	14	1	6	18	15.2	23
" 20	2	13	7	7	22	7	1	8	13	15.2	25
" 21	2	7	9	5	6	5	0	0	12	15.1	20
" 22	2	12	39	6	4	2	0	0	11	15.0	28
" 23	1	2	6	7	18	0	0	0	11	14.5	—
" 25	2	0	88	1	6	45	4	2	23	13.2	12
" 26	1	6	12	0	5	8	0	0	29	13.7	15
" 27	2	5	75	2	10	14	4	4	21	14.3	19
" 28	2	13	455	4	4	9	4	2	18	14.9	24
" 29	2	15	78	5	0	6	4	1	15	15.5	17
" 30	1	10	26	1	0	1	3	0	20	15.9	—
June 1	2	1	49	1	0	4	1	0	54	16.1	—
" 2	2	7	61	1	0	8	1	4	27	16.0	13
" 3	2	5	18	6	0	0	1	0	21	15.8	15
" 4	2	3	2	0	0	0	0	0	80	15.6	10
" 5	2	4	2	0	0	2	$\frac{1}{2}$	0	44	14.7	14

In interpreting the data obtained, several factors have to be taken into consideration. At high water, the water at the fishing station was always non-toxic during neaps, but often toxic during springs. At neaps, therefore, the fish caught were in a healthy condition, while at high water of springs they were sometimes netted in a dying condition. For this reason it is probable that the number of fish caught at about the time of high water springs was larger than it would have been in non-toxic water, although the length of time during which toxic water was present at the fishing station was short compared with the total length of time of fishing on any day. As the net used was relatively small, the numbers of smolts caught cannot be regarded as a reliable measure of the total number passing the fishing place in a given time. The greater the depth of water, the smaller was the fraction of the total area of cross-section represented by the area of the net. The ratio between the number of fish caught and the total number passing will thus be smaller at springs than at neaps. This ratio probably also depends to some extent on the strength of current, which is dependent on the tidal range and to some extent on the flow of fresh water from the upper reaches.

It has been stated that in some estuaries more fish are caught during springs than during neaps, as the strong currents running during springs stir up matter from the bottom, making the water opaque so that fish are unable to see and avoid

a net. Some determinations of opacity were made at the fishing station during the survey by observing the maximum depth at which a Secchi disc was just visible at high water of the daylight tide. The results are given in Table 62. The degree of opacity appeared to bear some relation to the tidal range, although no doubt it was influenced by the heavy fresh water floods which occurred from 31st May onwards. It is probable, however, that the changes in opacity were caused not so much by alterations in the amount of matter stirred up from the Estuary bottom as by the turbid waters from the central part of the polluted stretch which at high water during springs were carried upstream as far as the fishing station. There does not appear to be any obvious correlation between the numbers of smolts caught during a day-time fishing period and the opacity of the water.

In considering the variation in the total number of fish caught daily it must be remembered that since netting was carried out only at about the time of high water, the two daily fishing periods were sometimes both in daylight while sometimes one occurred during the night. A comparison of the numbers of fish caught in daylight hauls with the numbers caught on corresponding states of the tide on the following nights shows that approximately four times as many fish of all kinds were caught at night as during the day ; the corresponding ratio for smolts was 2 : 1. In calculating these ratios " night " has been regarded as the period between 9 p.m. and 4 a.m. (G.M.T.). A further complication arises from the fact that in general more fish were caught on the flood than on the ebb (Table 63).

TABLE 63—Relative Numbers of Fish Caught during the Ebb and Flood

Fish	Floods 2 hrs. before high water to high water		Ebbs High water to 2 hrs. after high water	
	No. of fish caught	Percentage of total no.	No. of fish caught	Percentage of total no.
Eels	233	89	28	11
Flounders	1,042	81	244	19
Sticklebacks	87	64	49	36
Salmon Smolts	172	58	123	42
Sea Trout Smolts	186	65	100	35
Total Smolts	358	62	223	38
Total fish	1,720	76	544	24

When a fishing period occurred partly in daylight and partly at night, it is to be expected that if the flood tide occurred during the dark period, a larger total number of fish would be caught than if the ebb had been fished in the dark. Some allowance must be made for this factor in considering Fig. 56, where the

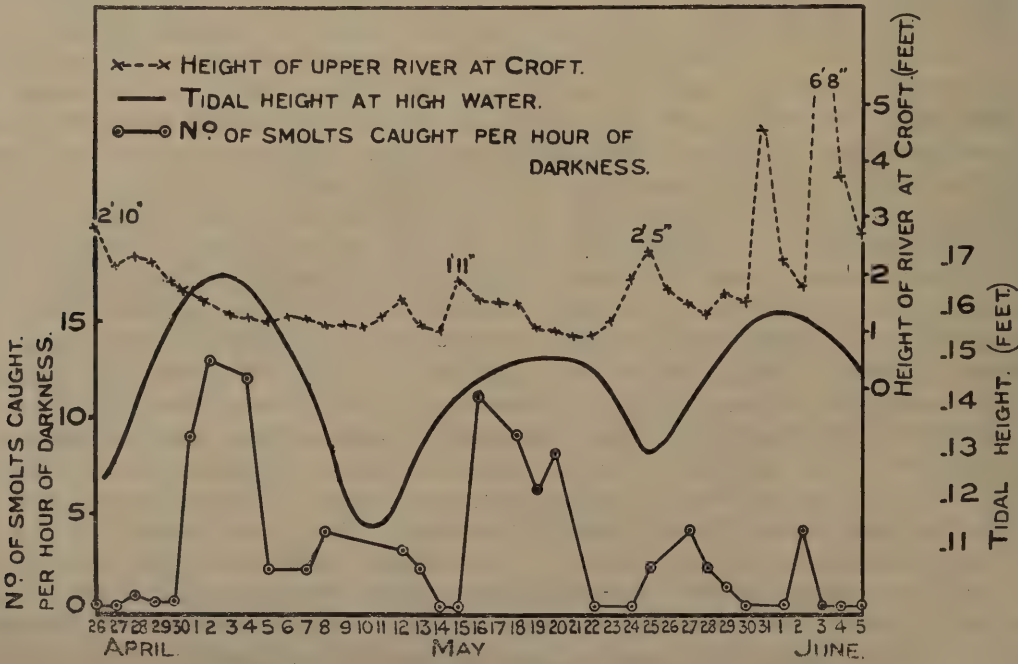


FIG. 56—Number of Smolts Caught at Thornaby Wood, 1931



numbers of smolts caught per hour of darkness on different days are compared with the corresponding height of the upper river and the tidal range. This graph does, however, show the variation in the numbers of fish caught under more or less comparable conditions, and the results may be compared with those obtained in a similar investigation on the Tay Estuary<sup>(3)</sup>. It will be seen that there is no obvious correlation between the height of the upper river and the number of smolts caught. On the other hand, there seems to be some correlation between the numbers and the tidal range. In view of the uncertainty with regard to the effect of the factors which have been discussed, however, it is not concluded that more fish were migrating at springs than at neaps. This conclusion would in any case be unjustifiable since, as will be shown later, smolts did not always pass the fishing berth and proceed directly down the Estuary to the sea, but in some cases remained for several days in the vicinity of the fishing station or even moved upstream above it. Reliable data with regard to smolt movements cannot be obtained without a much more intense investigation than was possible during the survey.

It will be seen from Fig. 56 that there was some similarity between the occurrence of smolts and of other common fish. Fair numbers of all kinds were caught on 28th April, a maximum was reached between 1st and 3rd May, and the numbers then fell away rapidly to 10th May. After this the correspondence was less clearly marked, but by 5th June only occasional fish of any sort were caught. On 28th May there was a very large catch of flounders, none of which appeared to be adult fish; no flounders netted were much greater in length than 4 in., and they were usually from 2 to 3 in.

Although there were so many flounders at the fishing station during the period of the smolt migration (the ratio of flounders to smolts was more than 2:1), the number found dead on the banks was very much smaller than the number of dead smolts recovered. It was thought that flounders might be less susceptible than smolts to cyanides, to which poison the death of fish in the Estuary was attributed. The experiments recorded in Table 64 were carried out

TABLE 64—*Relative Susceptibility of Flounders and Rainbow Trout to Potassium Cyanide*

Concentration of cyanide Gm. (CN) per 100,000 ml.	Time taken to overturn Min.		Temp. °C.	Dissolved oxygen concentration at beginning of experiment Per cent. of saturation
	Flounder	Trout		
0.015	72	72	14	78
0.0175	34	31	14	78
0.02	25	16	14	77
0.023	15	12	14	81
0.025	12	8	13	76
0.03	9	7	13	76

to decide this point. Since smolts were not available, rainbow trout were used. One flounder and one trout were exposed together to each solution of potassium cyanide. The time at which a flounder "overturned" was a little difficult to determine, unless the fish were prevented from settling on the bottom. The susceptibilities of flounders and trout to cyanides appear to be of the same order, and it is difficult to understand why more flounders were not found dead in the Estuary. It is possible, in view of the different habits of flounders and smolts, that of the fish killed, a larger proportion of the smolts than of the flounders was stranded on the Estuary banks and collected.

There appears to have been some general correlation between the numbers of smolts caught on any one day and the numbers found dead further down the Estuary either on the same or the following day, but the ratio between the two numbers was by no means constant. Thus on 13th May, 58 times as many smolts were picked up dead as were caught in the net, whilst on several occasions no dead smolts were found although average catches at Thornaby Wood were recorded. The ratio must be affected by the movements of the smolts after passing the fishing berth, by the efficiency of the netting and collection of dead smolts, by the position and intensity of the toxic stretch and probably by other

factors. There was no apparent correlation between the ratio and the height of the river at Croft, nor between this height and the actual number of dead smolts found.

All the smolts netted at Thornaby Wood were marked by inserting through the base of the dorsal fin silver wire carrying either one or two small glass beads, a different arrangement of colours being used for the fish caught on each tide. Some of these fish were subsequently recovered, either in the boom net or in a hand net, or were picked up dead on the banks of the Estuary. Their nett movements in the period between marking and recapture are recorded in Table 65.

TABLE 65—*Movements of Smolts in the Estuary*

Salmon Smolts		Sea Trout Smolts	
Interval between marking and recovery	Distance covered	Interval between marking and recovery	Distance covered
Days	Feet	Days	Feet
1	5,000 seawards	1	0
1	0	2	4,000 upstream
1	0	2	0
1½	5,000 seawards	3	1,000 upstream
2	23,000 seawards	4	4,000 seawards
9	0	9	32,000 seawards

These observations suggest that smolts move comparatively slowly through the Estuary, and this conclusion appears to be supported by the results of an investigation of the contents of the stomachs of smolts found dead at different positions in the Estuary. In 1931 every dead smolt picked up was opened and examined. In all, more than 3,000 salmon and 2,000 sea trout smolts were opened, and of these the percentages containing undigested food were 14·5 and 10·5 respectively. The proportion of the total number of smolts containing food was, however, markedly different above Stockton from below it. Above Stockton, 26 per cent., and below Stockton less than 1 per cent., contained food. Most of the dead smolts picked up were found in two fairly well defined areas. The upstream area stretched from above Thornaby Wood to Stockton Bridge, and the lower area from about Blue House Point to the Transporter Bridge. Between these areas few smolts were found, probably owing to the steep nature of the banks. The last position in the Estuary at which there is any considerable quantity of smolt food is at Thornaby Wood, 2 miles above Stockton Bridge. Of the group of dead smolts picked up in this region, about a quarter contained food. As the result of travelling only 3½ to 6 miles to the lower area from which smolts were recovered, almost all of them had by some means disposed of their food. There is no evidence that the food was regurgitated, since the fish that died in the lower reaches of the Estuary were killed by the same poison as those at Thornaby Wood. It seems reasonable to suppose, therefore, that either the processes of digestion are very rapid or that the migration through the Estuary is considerably slower than has previously been supposed<sup>(4)</sup>. There is no information on the rate of digestion by smolts, but some feeding experiments with similar food (*Gammarus pulex* L.) carried out at Barnard Castle on the closely related brown trout (*Salmo trutta* L.) showed that after 7 hours food was still easily recognisable and even after 12 hours digestion was incomplete.

The results of this work suggest that the migratory movements of smolts through the Tees Estuary are comparatively slow.

SOME CHARACTERISTICS OF MIGRATING SMOLTS

*Relation Between the Size, Age and Time of Migration*<sup>(5)</sup>

Information on the young stages of salmon and sea trout has hitherto been obtained mainly from readings of the scales of adult fish<sup>(4)(6)</sup>. Owing to protection by law and the commercial value of salmon and sea trout it is not ordinarily possible to obtain large numbers of smolts for direct examination. The survey of the Tees provided an opportunity for the examination of a large number of dead smolts picked up on the foreshore of the Estuary.



All fish examined were measured from the tip of the snout to the tip of the caudal fin and the lengths were recorded to the nearest quarter of an inch. In 1930 scales were taken for age determination from the first 236 fish and later from every eighth fish examined; in 1931 scales from every tenth fish were examined. All scales in 1930 and the salmon scales in 1931 were examined by the Scottish Fishery Board. An enlarged image of the scales was projected on to a screen and the age was determined from the annual rings of growth, according to the method of Dahl<sup>(7)</sup> and others. It has been shown by Dahl that the growth of scales is proportional to the growth of the fish. By a study of the scales and of the recorded length it is possible, therefore, to calculate the yearly growth of the fish.

The material for the study of the age of the migrating smolts in the Tees consisted of scales from 211 salmon and 266 sea trout in 1930, and 292 salmon and 187 sea trout in 1931. All the smolts examined were found to have spent two or three years in the river, the majority being two year old fish. A number of scales from both salmon and sea trout showed a series of open ridges at the growing edge, indicating that rapid growth had taken place just before they migrated. Table 66 shows the age distribution of salmon and sea trout smolts. By two year old fish are meant those showing two winter rings of growth, the second winter's growth being shown on the edge of the scale. Those designated 2+ had a ring of summer growth outside the second winter ring, showing that the third year's growth had begun. Three year old fish had 3 winter rings and 3+ fish a ring of summer growth outside the third winter ring, i.e. they had begun their fourth year's growth.

TABLE 66—*Age of Migrating Smolts*

Age of Smolts Years	Number of fish		Percentage of Total	
	1930	1931	1930	1931
Salmon				
2	145	140	69	48
2+	58	135	27	46
3	8	17	4	6
Total	211	292	100	100
Sea Trout				
2	137	65	52	35
2+	60	74	22	39
3	68	43	26	23
3+	1	5	—	3
Total	266	187	100	100

The percentage of salmon which migrate seaward at two years old in the Tees is comparable with that of the Tyne<sup>(8)</sup>, Wye,<sup>(9)</sup> Tweed, Forth and Findhorn, but different from that of the Spey and Don<sup>(10)</sup>. The percentage of sea trout smolts migrating at 2 years old is again similar to that of the Tyne, Tweed and Forth, but markedly different from that of the Findhorn, Spey and Don<sup>(6)</sup>. These comparisons are summarised in Table 67.

TABLE 67—*Percentage of Total Smolts Migrating at Two Years in Various Rivers*

River.	Percentage of salmon migrating at 2 years old.	Percentage of sea trout migrating at 2 years old.
Tees	95	74
Tyne	94	86
Wye	90	—
Tweed	97	79
Forth	90	68
Findhorn	92	15
Spey	71	29
Don	62	15

The length frequency curves for all salmon and sea trout smolts from the Tees measured in 1930 and 1931 are shown in Fig. 57. The numbers are plotted for half-inch groups and, for comparison with the results of other workers<sup>(4)(6)</sup>, a centimetre scale is also included. The number of salmon smolts measured in 1930 was 1,176 and the average length was 5·8 in. (14·7 cm.), with a range from 4½ to 8 in. (11·4 to 20·3 cm.). In 1931 the average length of 3,289 salmon smolts was 5·7 in. (14·5 cm.) with a range from 4¼ to 7½ in. (10·8 to 19 cm.).

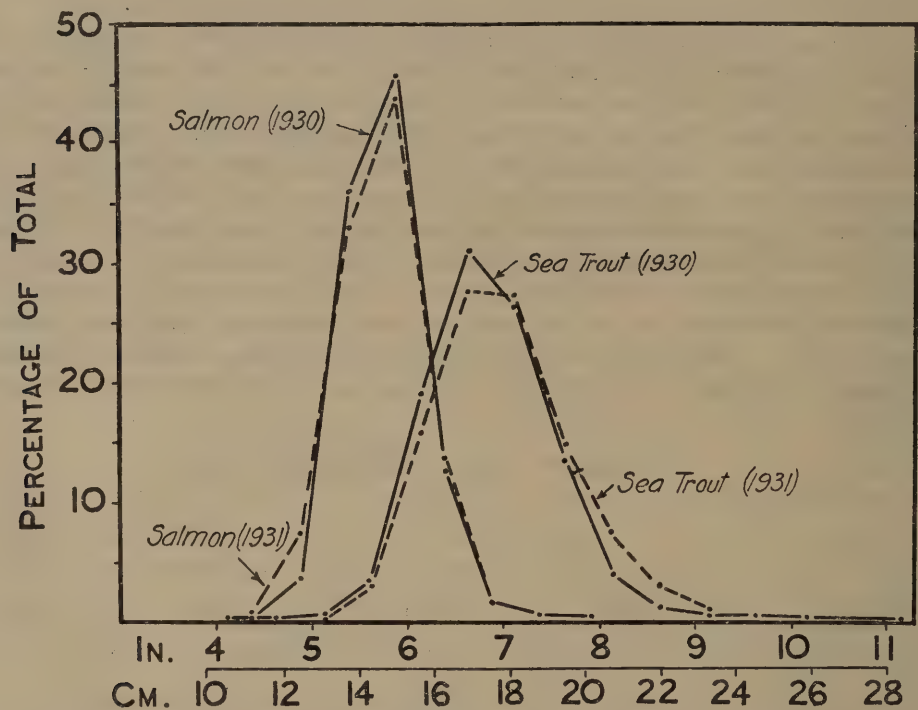


FIG. 57—Size Distribution of Salmon and Sea Trout Smolts, 1930 and 1931

Sea trout smolts were larger and had a greater range in both years. In 1930 the average length of 1,249 fish was 6·8 in. (17·3 cm.) and the range was from 4 to 11 in. (10·2 to 28 cm.). In 1931 the average length of 2,085 fish was 7 in. (17·8 cm.) and the range 5 to 9 in. (12·7 to 22·8 cm.). These figures include smolts of all ages.

The data given in Table 68 show the average sizes of the age groups in the two years. The three year old smolts were larger than the two year old in all cases, but their numbers were so small that they hardly affect the general average size.

TABLE 68—Average Length of Salmon and Sea Trout Smolts in the Tees

					1930.	1931.
Average length of all salmon smolts measured ..					5·8 in. (14·7 cm.)	5·7 in. (14·5 cm.)
" " of 2 year old " " ..					5·8 in. (14·7 cm.)	5·7 in. (14·5 cm.)
" " of 3 year old " " ..					6·7 in. (17·0 cm.)	5·9 in. (15·0 cm.)
Average length of all sea trout smolts measured ..					6·8 in. (17·3 cm.)	7·0 in. (17·8 cm.)
" " of 2 year old " " ..					6·8 in. (17·3 cm.)	6·9 in. (17·5 cm.)
" " of 3 year old " " ..					7·5 in. (19·0 cm.)	7·4 in. (18·8 cm.)

The number and proportion of smolts which showed extra growth increased as the season advanced. At the beginning there were very few which had any open ridges at the edge of the scales, but at the end of the migration period the



majority of the smolts examined showed some extra growth (Table 69). Why some fish at the end of the migration period showed no signs of extra growth is unknown, as there is little information on the movement of smolts in fresh water before they migrate.

TABLE 69—*Smolts showing Extra Growth at the Margin of the Scale*

Date when picked up	Salmon		Sea Trout	
	Total number examined	Percentage showing extra growth	Total number examined	Percentage showing extra growth
1930				
April 24—May 6	35	0	79	3
May 7—May 20	72	4	91	12
May 21—May 29	45	53	31	48
May 30—June 12	35	80	27	78
1931				
April 24—May 2	49	0	24	21
May 3—May 8	42	2	36	19
May 9—May 16	58	33	29	38
May 17—May 20	53	74	26	46
May 21—May 24	29	72	7	29
May 25—June 2	61	90	65	65

In view of the increase in the proportion of smolts which had grown rapidly as the season advanced it might have been expected that the average size of the smolts at the beginning of the season would have increased at the end. The salmon smolts of 1931 showed a slight increase in average size but neither the salmon of 1930 nor the sea trout of either year showed any such growth (Table 70). Further,

TABLE 70—*Length of Salmon and Sea Trout Smolts throughout the Migration Period*

Period	Salmon		Sea Trout	
	Number	Average length of total 2 year old fish (2 and 2+) In.	Number	Average length of total 2 year old fish (2 and 2+) In.
1930				
April 24—May 6	33	5.8	51	6.8
May 7—May 20	70	5.9	67	7.0
May 21—May 29	45	5.9	28	6.6
May 30—June 12	34	5.8	24	6.8
1931				
April 24—May 2	39	5.5	13	6.9
May 3—May 8	41	5.6	26	6.7
May 9—May 16	54	5.8	24	7.0
May 17—May 20	51	5.8	19	7.0
May 21—May 24	29	5.7	5	6.9
May 25—June 2	61	5.9	52	6.8

the average length of those smolts which had grown during the spring of the migration year was not significantly different from that of those which showed

no extra growth (Table 71). It follows therefore that those smolts which delayed their migration until they had made some extra growth had been, on the average, smaller at the beginning of the migration period than those which migrated without further growth. Calculations, from the scales, of the size at the end of the second winter show that on the whole the smallest smolts waited longest and made most further growth before they migrated (Table 72).

TABLE 71—Average Length in Inches of Smolts with and without Second Year Spring Growth

Age	Salmon		Sea Trout	
	1930	1931	1930	1931
2 years	5·8	5·7	6·8	7·0
2+ years	5·8	5·8	6·8	6·9

TABLE 72—Increase in Length of Salmon and Sea Trout Smolts after their Second Winter

Period .	Number examined	Average size at end of 2nd winter Inches	Average size at migration Inches	Amount of growth made after end of 2nd winter Inches
SALMON				
1930				
April 24—May 6	0	—	—	—
May 7—May 20	3	5·2	5·8	0·6
May 21—May 29	24	5·2	5·9	0·7
May 30—June 12	28	5·1	5·8	0·7
1931				
April 24—May 2	0	—	—	—
May 3—May 8	1	5·0	5·5	0·5
May 9—May 16	19	5·3	5·9	0·6
May 17—May 20	39	5·1	5·7	0·6
May 21—May 24	21	4·9	5·6	0·7
May 25—June 2	55	5·0	5·9	0·9
SEA TROUT				
1930				
April 24—May 6	2	6·0	6·6	0·6
May 7—May 20	11	6·1	6·9	0·8
May 21—May 29	14	5·8	6·7	0·9
May 30—June 12	21	6·1	6·9	0·8
1931				
April 24—May 2	5	6·3	6·8	0·5
May 3—May 8	7	5·4	6·2	0·8
May 9—May 16	11	6·2	7·0	0·8
May 17—May 20	11	6·5	7·1	0·6
May 21—May 24	2	5·9	6·8	0·9
May 25—June 2	38	5·9	6·9	1·0



It appears therefore that smolts reach a certain size before migrating. Those smolts which formed the 2+ group were, at the beginning of the migration period, too small to have a strong impulse to leave the river; as a result of the increased food supply in the spring they later made sufficient growth to bring them to the normal size at which smolts migrate. The frequency curves for the length of two year old migrants and the 2+ group at the end of the second winter are shown in Figs. 58 and 59 for salmon and sea trout respectively. The curves, while similar in form, are distinctly separate, the difference in modal size being about 0.75 in. in the case of salmon and 1 in. in the sea trout.

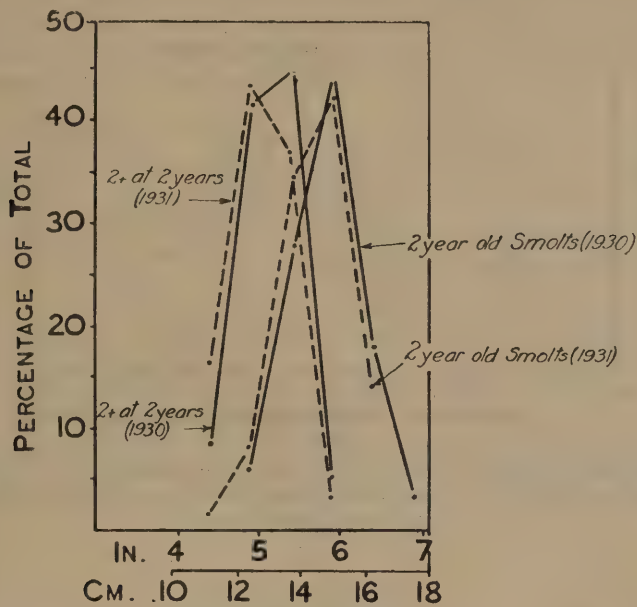


FIG. 58—Comparison of Lengths of 2 year old Salmon Smolts with Estimated Lengths of 2+ Smolts at 2 Years

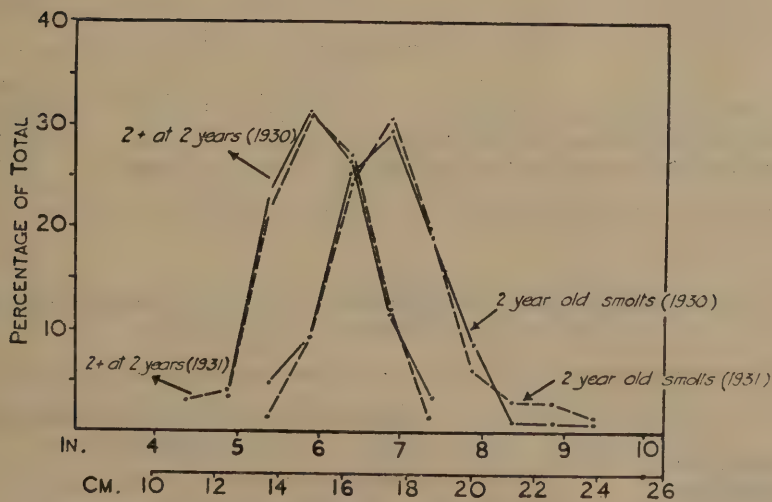


FIG. 59—Comparison of Lengths of 2 Year Old Sea Trout Smolts with Estimated Lengths of 2+ Smolts at 2 Years

The relationship between time of migration and size is even clearer with fish which migrate at three years old, as has been pointed out by Nall<sup>(6)</sup> and Menzies<sup>(4)</sup>. The calculated size of these smolts at two years old is considerably smaller than the migration size of two year old smolts (Table 73). The number of three year old smolts examined was small. In 1930 there were 8 salmon and 68 sea trout, and in 1931, 17 salmon and 43 sea trout. The frequency curve for size for the largest

sample (three year old sea trout smolts migrating in 1930) is shown in Fig. 60 ; the curves for the other groups of three year olds show similar relations.

Measurements indicate that smolts which migrate in their third year are smaller also at the end of their first year than those which migrate in their second year (Table 74).

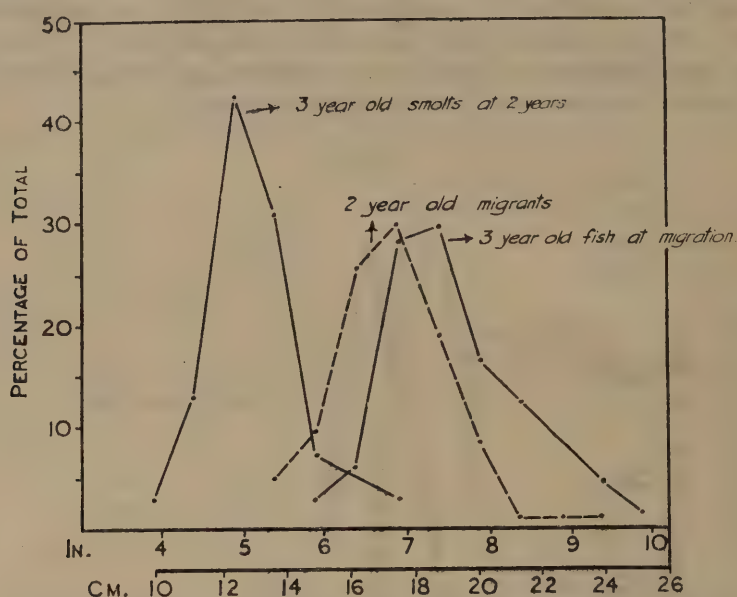


FIG. 60—Lengths of Sea Trout Smolts migrating at 3 Years, compared with their Estimated Length at 2 Years and the Length of 2 Year Old Migrants

TABLE 73—Length of Two Year Old Smolts at Migration and of Three Year Old Migrants at the End of their Second Year

	Salmon		Sea Trout	
	1930	1931	1930	1931
Observed average length of 2 years old migrants	Inches 5·8	Inches 5·7	Inches 6·8	Inches 6·9
Calculated average length of 3 year old fish at 2 years	4·4	3·9	5·1	4·4
Observed average length of 3 year old fish at 3 years	6·7	5·9	7·5	7·4

TABLE 74—Size at End of First Year's Growth of 2, 2+, and 3 year old Migrating Smolts

No. of years growth at migration	Calculated length at end of 1st year's growth Inches			
	Salmon migrating in		Sea Trout migrating in	
	1930	1931	1930	1931
3	1·6	1·5	2·0	2·0
2+	1·9	2·0	2·4	2·5
2	2·1	2·2	2·6	2·7

While this work does not explain the factors which bring about the seasonal migration of smolts, it appears that one condition that must be satisfied before they can begin their seaward movement is that they must have attained some physiological condition associated with a definite minimum size.



Sex of Migrating Smolts<sup>(5)</sup>

There are no secondary sexual characters in smolts which can be used to determine the sex, and it was therefore necessary to examine the gonads. The difference between the testes and ovaries was obvious to the naked eye, the testes being smooth and white and the ovaries yellow and granular. Male salmon smolts fell into two well-defined groups, in one of which the testes were very small and in the other they were large and well developed ; this difference occurred in fish of the same size throughout the length range. For convenience the males have been designated as ♂1 for those with small testes and ♂2 for those with large testes. These seemed to be definite classes, for it was seldom that there was any difficulty in deciding to which group the smolt belonged. This phenomenon was not characteristic of sea trout males, there being only 4 which were doubtfully designated as ♂2.

In both salmon and sea trout there was a large preponderance of females, the ratio of females to males in salmon being 1.93 and in sea trout 2.77. Meek<sup>(8)</sup> found ratios of 1.70 and 1.64 for salmon and sea trout smolts picked up dead in the Estuary of the Tyne. The mean size of the two sexes did not differ in either case by more than 0.1 in., a difference which cannot be considered significant.

In the salmon smolts the proportion of males which were classed as ♂2 was 27.3 per cent. The ♂2's were, in general, larger than ♂1's (Table 75).

Most of the ♂2 group migrated early in the season. The change in proportion as the spring advanced is shown in Table 76. It is possible, therefore, that the state of development of the gonads may have some connection with the time of migration, but further work would be necessary before any definite conclusions could be drawn.

TABLE 75—Extent of Sexual Development of Male Salmon Smolts Migrating through the Tees Estuary

Length Inches	Total number of males examined	Percentage of Total number designated as ♂2
4—4 $\frac{3}{4}$	13	15.4
5—5 $\frac{3}{4}$	506	22.9
6—6 $\frac{3}{4}$	392	32.1
7—7 $\frac{3}{4}$	7	100.0

TABLE 76—Difference in the Extent of Sexual Development of Salmon Smolts throughout the Migration Period

Date of migration	Male Smolts designated as ♂2 Percentage of Total number examined
April 24—May 8	48.0
May 9—May 20	28.0
May 21—June 2	17.0

Food of Smolts<sup>(5)</sup>

The smolts examined were entirely carnivorous. By far the greater number contained one or more specimens of *Gammarus duebeni* (Lilljeborg) ; the percentage of feeders containing this organism were 67.0 for salmon and 70.0 for sea trout. Larvae of the *Heptageniidae*, *Ecdyonurus* and *Rhithrogena*, and the Trichopterous

larvæ *Hydropsyche* sp. and *Leptocerus* sp. were also common. Many other organisms occurred, and a list of those found more than once is given in Table 77.

TABLE 77—*Organisms Found in Smolts Migrating through the Tees Estuary*

Food organism	Percentage of Smolts in which the food occurred	
	Salmon	Sea Trout
<i>Gammarus duebeni</i>	67	70
Chironomid larvae	12	12
Heptageniid larvae	13	5
<i>Hydropsyche</i> sp. larvae	13	9
Trichopterous larvae indet.	5	9
<i>Perla</i> sp. larvae	2	3
<i>Leptocerus</i> sp. larvae	3	3
<i>Baetis</i> sp. larvae	2	—
Adult Trichoptera	2	—
<i>Leuctra</i> sp. larvae	1	—
Coleoptera	1	6
<i>Hydroptila</i> sp. larvae	1	—
Limnophilid larvae	1	—
<i>Ephemerella</i> sp. larvae	1	—
Adult Diptera ..	1	1
<i>Hydrobia jenkinsi</i>	—	2
Others	3	4

“ Others ” included Caddis pupae, *Asellus aquaticus*, *Corixa*, *Tanytarsus* sp. larvae, Tipulid larvae, *Chloroperla grammatica* larvae, Hemiptera, *Polycentropus* sp. larvae, Chironomid pupae, earwigs, *Gyrinus* larvae, and *Amphinemura* sp. larvae.

Collections in the area in which the smolts were feeding showed that the frequency of occurrence of the common organisms was very similar to that found in the fish, and it seems, therefore, that smolts of both salmon and sea trout, like the brown trout,<sup>(11)</sup> feed indiscriminately on any convenient animal organism.

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CHAPTER XV

EFFECT OF POISONS ON SOME INVERTEBRATE ANIMALS

Certain species of the marine invertebrate fauna were found to penetrate into less saline water in the estuaries of the Tay and Tamar than in the polluted Tees. In order to determine whether this difference was in any way due to the presence of direct poisons in the middle reaches of the Tees Estuary experiments were made on six species of crustaceans, four of which have a greater range or are more abundant in the two unpolluted estuaries and two of which have a similar range in all three.

*Crangon vulgaris*, the common shrimp, living in bowls of water with a salinity above 12 gm. per 1,000 gm., withstood low concentrations of dissolved oxygen and tolerated phenol in a concentration of 1 gm. per 100 litres for a period of 25 days. Fig. 61 shows the results of experiments in which four shrimps were placed in each of a series of bowls containing water of different salinities and cyanide

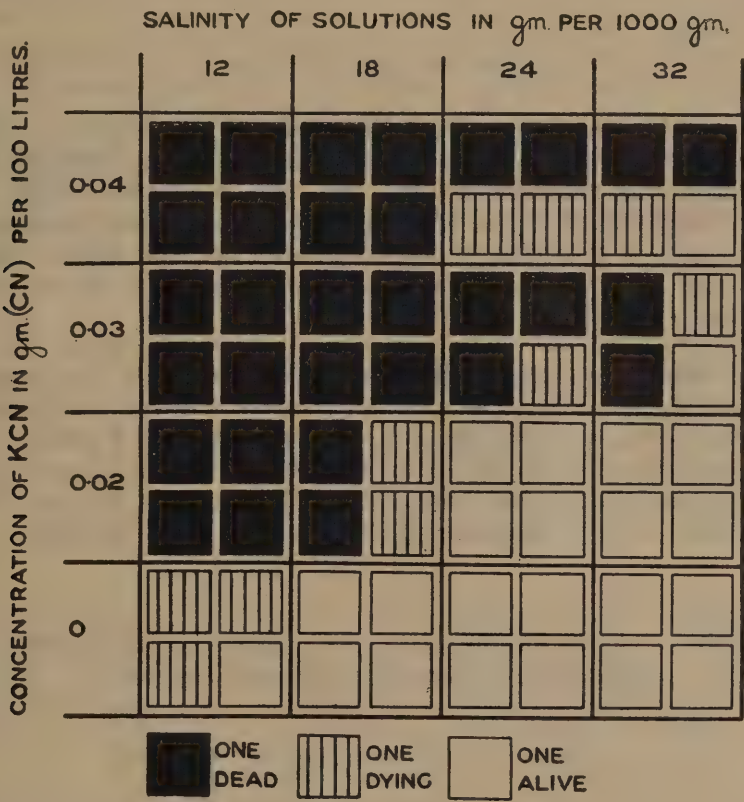


FIG. 61—Effect, after 17 hours, of Potassium Cyanide, in Water of Different Salinities, on the Common Shrimp (*Crangon vulgaris*) (Temp. about 3° C.)

contents. The shrimps died in brackish water of a salinity similar to that found in the central reaches of the Tees Estuary and containing cyanide in a concentration of 0.02 gm. (CN) per 100 litres, a concentration which occurred frequently in the Estuary. A second series of similar experiments showed that shrimps were affected by cyanide in concentrations as low as 0.01 gm. (CN) per 100 litres, and that their susceptibility increased with decreasing salinity of the water.

*Praunus flexuosus*. Similar experiments were made with mysids, mainly *Praunus flexuosus* with some individuals of other species. The results shown in Table 78 indicate that these animals are affected by a concentration of 0.02 gm. (CN) per 100 litres, and suggest that they, like shrimps, are more susceptible to cyanide in water of low salinity.

TABLE 78—*Numbers of Mysids Surviving in Solutions of Potassium Cyanide in Waters of Different Salinities*

Experiment A	Concentration of cyanide 0·02 gm. (CN) per 100 litres				Controls (without cyanide)			
Salinity of solutions in gm. per 1,000 gm.	5	10	15	30	5	10	15	30
Number of mysids :—								
Originally present .. .. .	6	6	6	6	6	6	6	6
Surviving on the 6th day .. ..	0	0	2	3	4	5	4	6

Experiment B	Concentration of cyanide Gm. per 100 litres				Controls (without cyanide)			
	0·01	0·02						
Salinity of solutions in gm. per 1,000 gm.	10	12	15	20	10	12	15	20
Number of mysids :—								
Originally present .. .. .	5	5	5	5	5	5	5	5
After 2 days .. .. .	4	1	2	2	5	5	5	5
After 7 days .. .. .	4	0	1	2	5	5	5	4

*Gammarus marinus*.—Twenty breeding females and twenty males were kept in each of three bowls for 44 days. The water had a salinity between 25 and 32 gm. per 1,000 gm. and was renewed daily. To one bowl was added cyanide in a concentration of 0·02 gm. (CN) per 100 litres, and to another the same concentration of cyanide with, in addition, 0·02 gm. phenol per 100 litres. The third bowl served as a control. No difference was observed between the rates of mortality in the three bowls.

*Corophium volutator*.—Table 79 shows the results of an experiment with this mud-burrowing crustacean, which has a more limited range of distribution in the Tees Estuary than in the estuaries of the Tay and Tamar. The solutions were renewed daily except on the 2nd, 5th, 9th and 11th days. This organism is resistant to cyanide in a concentration of 0·02 gm. (CN) per 100 litres, but cannot long survive a concentration of 0·1 gm. (CN) per 100 litres.

TABLE 79—*Numbers of Corophium volutator Surviving in Solutions of Potassium Cyanide in Waters of Different Salinities*

			Concentration of potassium cyanide Gm. (CN) per 100 litres						Controls (without cyanide)		
			0·1			0·02					
Salinity of solutions gm. per 1,000 gm. .. ..			5	15	30	5	15	30	5	15	30
Numbers of Corophium											
Originally present .. ..			8	8	8	8	8	8	8	8	8
After 3 days .. ..			0	2	1	7	7	8	8	6	7
After 15 days .. ..			0	0	0	7	7	8	7	6	6

*Carcinus maenas* (shore crab).—This species is found in the most polluted reaches of the Tees and extends to approximately the same relative distance from the sea as in the unpolluted Tay and Tamar. Five small specimens were placed in each of two bowls containing water of salinity 10 gm. per 1,000 gm., which is the average salinity of the water near the limit of the distribution of the species. To one bowl, 0·02 gm. (CN) per 100 litres was added, and the water



in both bowls was renewed daily for 14 days. No deaths occurred in either the control or the cyanide solution. It is an interesting observation that the crabs reduced the dissolved oxygen to a greater extent in the control than in the cyanide solution. Further experiments showed that shore crabs, or at least some individuals of the species, are remarkably resistant to high concentrations of cyanide (Table 80).

TABLE 80—Numbers of the Shore Crab, *Carcinus maenas*, Surviving after 20 Hours in Solutions of Potassium Cyanide in Water of Salinity 10 gm. per 1,000 gm.

	Concentration of potassium cyanide Gm. (CN) per 100 litres			
	1.5	1.0	0.5	0
Alive after 20 hours	1	1	1	3
Dead after 20 hours	2	2	2	0

*Eurytemora hirundoides*.—This planktonic copepod, which is widely distributed in the Tees Estuary, was found to survive for a week in bowls of water of salinities between 2 and 25 gm. per 1,000 gm., but to die off more rapidly in waters of lesser or greater salinity. It was found to be very resistant to cyanide, concentrations between 0.03 and 0.02 gm. (CN) per 100 litres having no appreciable effect under the conditions of the experiment. The results are shown in Table 81.

TABLE 81—Percentages of *Eurytemora* surviving in Solutions of Potassium Cyanide in Waters of Different Salinities

	Concentration of potassium cyanide Gm. (CN) per 100 litres								Controls (without cyanide)			
	0.03				0.02							
Salinity of solutions gm. per 1,000 gm. ..	1	7	15	25	1	7	15	25	1	7	15	25
Numbers of Eurytemora originally present ..	42	43	41	44	42	40	41	41	38	36	39	38
Percentage surviving :												
6th day .. ..	81	93	78	70	81	88	90	68	82	94	87	84
11th day .. ..	24	49	37	41	38	53	44	39	24	47	59	55
16th day .. ..	2	21	0	14	0	8	12	15	3	8	23	24

Of the six species of crustacea examined, two only, Crangon and Praunus, were poisoned by cyanide in concentrations at or below 0.02 gm. (CN) per 100 litres. There is some evidence that their susceptibility is greater in water of low salinity. It may be assumed that they are likely to encounter toxic conditions in the Tees Estuary. Both were widely distributed and were found relatively as far up towards the head of the Tees Estuary as they were in the Tay and Tamar, but they were much less abundant in the Tees. Their susceptibility to cyanide poisoning may explain their scarcity in the central reaches of the Tees.

The other four species of crustacea, in their adult stage, are more resistant to cyanide and are not likely to encounter lethal concentrations in the Tees Estuary. The shore crab and the planktonic copepod *Eurytemora* are abundant and widely distributed in the Tees. Gammarus and Corophium have a much smaller range

in the Tees than in the Tay and Tamar (Fig. 62) ; these animals, at least in their adult stages, appear to be able to withstand the concentrations of cyanide in the Tees and their limited range must be attributed to some other factor.

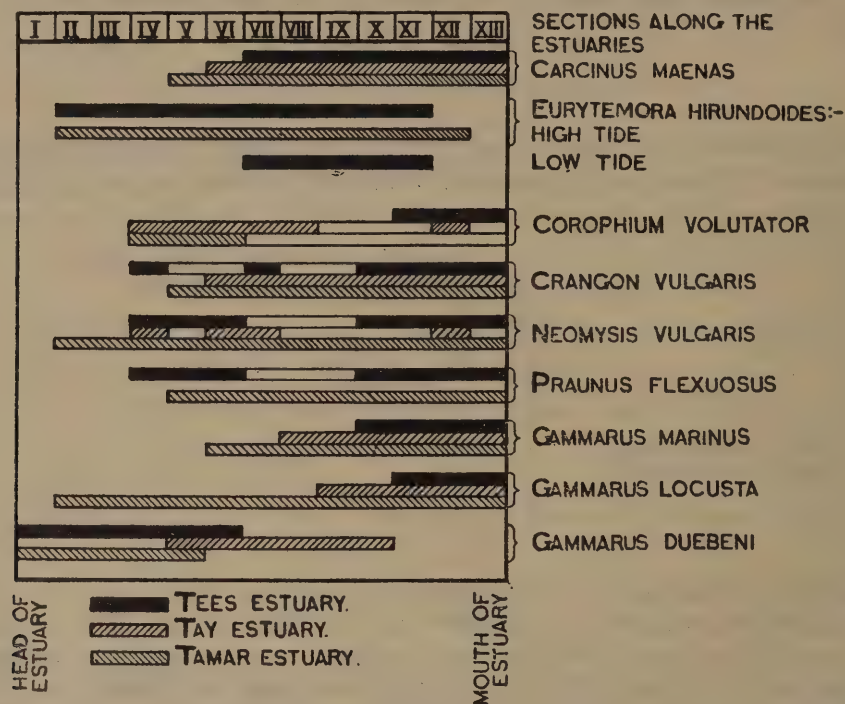


FIG. 62—Distribution of Certain Species of Crustacea in the Estuaries of the Tees, Tay and Tamar



## CHAPTER XVI

## CHEMICAL CHANGES IN INDUSTRIAL EFFLUENTS AFTER THEIR DISCHARGE INTO THE ESTUARY

If an effluent is discharged into a fresh water stream and the volume of the effluent and the rate of flow of the stream are known, the concentration of the effluent at a point sufficiently far from the outfall to allow of complete mixing may be calculated. The estimation of the effect of a series of effluents on the waters of the Tees Estuary is a much more difficult problem. Here, in place of a stream, there is a long stretch of water moving to and fro under tidal action and changing in volume with the tidal height and range. Fresh water is continuously entering the upper end of this reservoir, and at the lower end brackish estuary water passes out to sea on the ebb and sea water flows in on the flood. If the substances discharged into the Estuary were soluble and chemically stable, their concentration in the general body of the Estuary waters would attain and remain at the value resulting from their dilution with the incoming water from the upper river and the sea. If, however, the substances discharged were decomposed after their dilution with the waters of the Estuary, their concentration would be lower than that given by this simple relationship, the difference depending on their rate of decomposition and the length of time they spent in the Estuary. Before comparing the estimated and observed concentrations of constituents of industrial effluents in the Estuary, it is necessary therefore to estimate the time taken by their passage to the sea and the extent of their decomposition during this period.

The length of time spent by fresh water in the Estuary before being finally discharged into the open sea was discussed in Chapter III. It was estimated that about 7 days were required for water to travel from Stockton to the mouth of the Estuary during dry summer weather, and about  $2\frac{1}{2}$  days under normal winter conditions. The main toxic effluents are discharged between Newport and Cargo Fleet (9 miles and  $5\frac{1}{4}$  miles from the open sea), and the length of time spent by these effluents in the Estuary was estimated to vary between 2 and 5 days for discharges at Newport and between 1 and  $1\frac{1}{2}$  days for effluents discharged at Cargo Fleet. In considering the effect of effluents upon the Estuary water, therefore, their decomposition during periods of this order is of importance.

The general method adopted in determining the stability of a solution of an effluent or toxic substance was to keep a volume of 20 litres in a large open vessel and observe its toxicity to rainbow trout at intervals of one or more days. Usually determinations of dissolved oxygen concentration and temperature and sometimes pH value were made at the same time. The results of tests in which the dissolved oxygen concentration fell to an amount insufficient to support fish life were rejected. The effect of temperature on the rate of decomposition of effluents and their constituents was not investigated. Where, however, the rates of decomposition of two substances or of one substance under different conditions are compared, the data on which the comparison is based were obtained from experiments carried out at approximately the same temperature.

## DECOMPOSITION OF SPENT STILL LIQUORS AND OF PURE PHENOLIC SUBSTANCES

Since it is difficult to obtain standardised solutions of the tar acids present in spent still liquors and in effluents from coke oven gas coolers, it was necessary to work with a simple phenolic substance typical of the group, and for this purpose *p*-cresol was chosen. The mode of action of this substance on fish (Chapter XIII) is similar to that of phenol (the most important simple phenolic constituent of tar acids), and *p*-cresol is preferable to phenol as an experimental poison since its toxic action on individual fish varies less than that of phenol.

*Effect of Sewage*<sup>(1)</sup>

The results of two comparable experiments giving the rate of loss of toxicity of *p*-cresol and of a sample of spent still liquor diluted with tap water containing

varying concentrations of sewage are shown in Table 82. Portions of the same sample of sewage were used in both Series 1 and Series 2. The acceleration produced by increasing concentrations of sewage in the rate of decomposition of both *p*-cresol and the tar acids of the effluent was very marked. It is of interest to note the comparatively low concentrations of dissolved oxygen to which the test fish were subjected without injury in the solutions containing high concentrations of sewage.

TABLE 82—*Effect of Sewage on Rate of Loss of Toxicity of p-Cresol and of a Spent Still Liquor*

Concentration of sewage Per cent.	<i>p</i> -Cresol : 0·8 gm. per 100 litres				Spent still liquor : $\frac{1}{2}$ per cent.			
	No. of days to become non-toxic		Minimum oxygen recorded Per cent. of saturation value		No. of days to become non-toxic		Minimum oxygen recorded Per cent. of saturation value	
	Series 1	Series 2	Series 1	Series 2	Series 1	Series 2	Series 1	Series 2
0	49	50	79	77	32	35	77	63
$\frac{1}{4}$	11	11	72	70	27	18	72	58
$\frac{1}{2}$	9	9	54	54	17	11	66	59
1	7	6	52	36	11	10	51	41
$1\frac{1}{2}$	6	6	45	45	10	10	38	35

In another series of experiments the rate of decomposition of phenolic substances when diluted, mixed with sewage, and incubated in sealed bottles was studied by observing the rate of absorption of dissolved oxygen from the solution. The weights of dissolved oxygen absorbed by two samples of a spent still liquor (Effluent No. 154) when diluted with tap water containing sewage and incubated at 18·3° C. are shown in Table 83.

TABLE 83—*Weight of Dissolved Oxygen Absorbed in Five Days by Two Samples of a Spent Still Liquor Diluted with Tap Water Containing Sewage and Incubated at 18·3° C.*

Concentration of spent still liquor Per cent.	Concentration of sewage Per cent.	Approximate concentration of tar acids in solution Parts per 100,000	No. of days incubated	Dissolved oxygen absorbed (parts per 100,000 of the solution) by		
				Sewage	Sewage plus spent still liquor	Spent still liquor (by difference)
0·33	0·5	0·8	1	0·02	0·18	0·16
			2	0·04	0·54	0·50
			3	0·06	0·62	0·56
0·5	0·5	1·3	1	0·02	0·05	0·03
			2	0·05	0·28	0·23
			3	0·06	0·69	0·63
			4	0·08	0·80	0·72

The extent to which phenol and *p*-cresol are oxidised when diluted with water containing sewage and incubated in sealed bottles at 18·3° C. for 5 days is shown in Table 84.



TABLE 84—Dissolved Oxygen Absorbed in Five Days by *p*-Cresol and Phenol in Solutions Containing Sewage

Concentration of <i>p</i> -cresol	Dissolved oxygen absorbed : parts per 100,000 of solution containing		
Gm. per 100,000 ml. of solution	1 per cent. sewage (Sample A)	1 per cent. sewage (Sample B)	0.5 per cent. sewage (Sample C)
0	0.39	0.38	0.44
0.04	0.43	—	—
0.06	0.46	—	—
0.10	0.52	—	0.65
0.20	0.68	0.62	0.78
0.30	—	—	0.92
0.40	—	0.82	1.08

Concentration of phenol	Dissolved oxygen absorbed : parts per 100,000 of solution containing	
Gm. per 100,000 ml. of solution	0.75 per cent. sewage (Sample D)	0.75 per cent. sewage (Sample E)
0	0.04	0.46
0.1	0.21	0.59
0.2	0.26	0.76
0.5	0.28	0.95
1.0	0.42	—

If it is assumed that the sewage mixed with the phenolic substance is oxidised to the same extent as the duplicate sample of sewage incubated alone, the dissolved oxygen absorbed by the phenol can be calculated. The value of the oxygen absorbed by *p*-cresol and phenol has been calculated in this way from the data given in Table 84. In Fig. 63 the observed weight of oxygen absorbed from

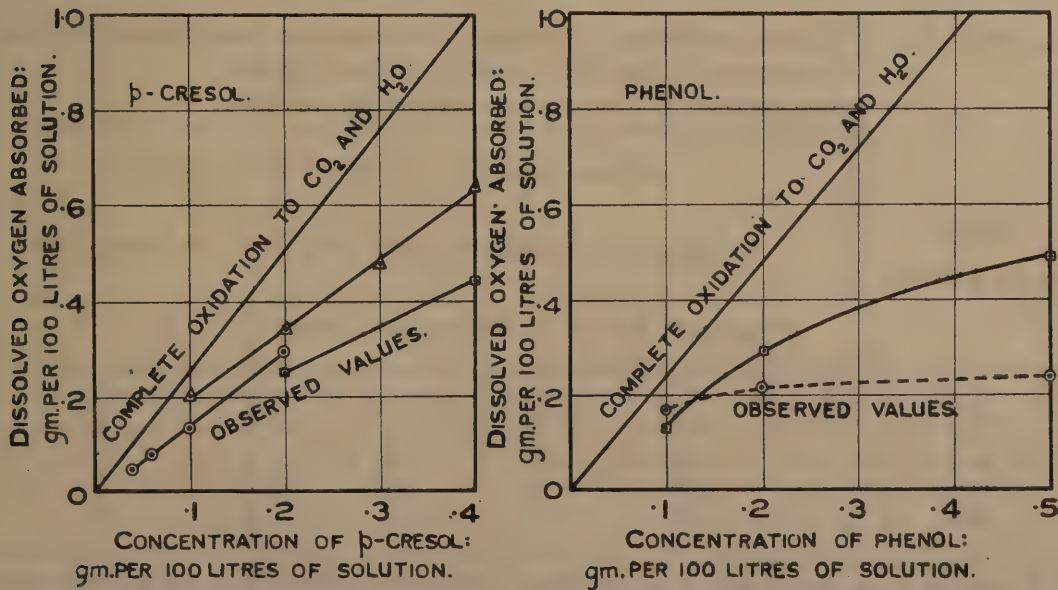


FIG. 63—Dissolved Oxygen absorbed in 5 Days by *p*-Cresol and Phenol from Solutions containing Sewage

solution by the phenol and cresol are compared with the weight of oxygen necessary for their complete oxidation to carbon dioxide and water. *p*-Cresol appears to be more readily oxidised by bacterial action than phenol; the weight of oxygen absorbed in 5 days by the cresol from solutions containing sewage is about one-half of the value necessary for its complete oxidation to carbon dioxide and water.

It appears that tar acids in the concentrations in which they occur in the Tees Estuary (up to 0.05 part per 100,000) do not inhibit the biological oxidation of organic matter but are themselves oxidised at the expense of the dissolved oxygen of the Estuary waters. The ability of sewage bacteria to decompose the constituents of spent still liquors, including tar acids, is well known; similar effluents have been purified on a large scale on biological filters initially seeded with sewage.

Experiments on the toxicity to fish of mixtures of poisons (Chapter XIII) showed that the physiological action of *p*-cresol on fish was different from that of 1.2.6.xylenol, and it is interesting to note that the effects of sewage on the rate of decomposition of these two substances also appeared to be different. The decomposition of aqueous solutions of *p*-cresol was greatly accelerated by addition of sewage, but the rate of decomposition of 1.2.6.xylenol was not similarly increased (Table 85).

TABLE 85—*Rate of Decomposition of 1.2.6.Xylenol in Solutions Containing Different Concentrations of Sewage*

Initial concentration of xylene: 1.5 gm. per 100 litres

Sewage Per cent.	No of days required for solution to become non-toxic to trout
0	4
0.25	4
0.5	6
0.75	4
1	6
1.5	5

#### *Effect of Salinity*

The rate of decomposition of *p*-cresol in solutions of tap water containing sewage and various concentrations of "sea salt," and in Estuary water of varying salinity is shown in Table 86. On the whole, the rate of decomposition was slower the higher the concentration of salt. The retardation in the disappearance of toxicity caused by increasing the salinity was accompanied by a reduction in the rate of absorption of dissolved oxygen from the solution. A similar retarding effect of sodium chloride on the rates of decomposition of sewage and of sewage mixed with industrial effluents and incubated in sealed bottles is described in Chapter XVII.

TABLE 86—*Rate of Decomposition of Solutions of p-Cresol in Tap Water Containing Sewage and "Sea Salt" and in Estuary Water*

Initial concentration of *p*-cresol: 0.8 gm. per 100 litres

Salinity Gm. per 1,000 gm.	No. of days required for solution to become non-toxic		
	In tap water containing "sea salt" and		In Estuary water
	0.5 per cent. sewage	0.25 per cent. sewage	
3.4	5	6	2
11.8	5	3	3
20.0	6	4	3
23.2	8	7	5
25.6	12	7	5

Under comparable conditions the rate of decomposition of *p*-cresol was higher in Estuary water than in tap water mixed with sewage. The rate of absorption of dissolved oxygen by a spent still liquor diluted with Estuary water and incubated



in a sealed bottle was also greater than when the diluent was sewage diluted with tap water (Chapter XVII). The decomposition of *p*-cresol and of spent still liquors in which the most toxic constituents are tar acids can be effected by the action of bacteria, and it is known that bacteria capable of causing this decomposition are present in sewage. It appears, however, that there is in the Estuary and not in diluted sewage some factor capable of accelerating the breakdown of phenolic substances. This acceleration does not seem to be due to inorganic salts nor to an optimum condition of hydrogen ion concentration. It is possible that the high rate of decomposition in the Estuary is due to the presence of a specially active bacterial flora. The amount of decomposition which occurs when tar acids are diluted with tap water containing sewage, whilst not so great as that obtained with Estuary water as diluent, is nevertheless considerable. It can hardly be doubted that the discharge of sewage into the Estuary accelerates the decomposition of tar acids.

It is evident that, during the period of about 1 to 5 days for which tar acids may remain in the Estuary, a considerable reduction, if not a complete loss, of toxicity occurs. The presence in the Estuary of a large volume of water which remains there for several days tends therefore to reduce the general concentration of tar acids below the value estimated from the amount of dilution afforded by the new fresh and salt water entering the Estuary every day.

DECOMPOSITION OF EFFLUENTS FROM GAS SCRUBBERS AND OF PURE CYANIDES

In comparing the rate of decomposition of a substance under different conditions by observations of the change in its toxicity to fish, considerable variations in the results may be expected, since the difference between the resistance of individual test fish to poisons may be large. Moreover, in solutions containing approximately equal concentrations of sewage the dissolved oxygen content may fall at a different rate, either because of small differences in the composition of the sewage used or because of inequalities in temperature; thus, since the toxicity of a direct poison, as determined by its effect on fish, is affected by the degree of oxygenation of the solution, a further source of variation in the results is introduced. The time taken by solutions of potassium cyanide in tap water with added sewage, stored under similar conditions, to become non-toxic is given in Table 87. The temperature during Series 1 was higher than during Series 2. From these figures it appears that the effect of a given factor can only be regarded as significant if it causes a larger variation than 2 days in 7 in the time taken by a solution of cyanide to become non-toxic.

TABLE 87—*No. of Days Required for Solutions of Potassium Cyanide in Tap Water containing Sewage to become Non-toxic*

Concentration of cyanide: 0.04 gm. (CN) per 100 litres  
Diluent: tap water containing 0.5 per cent. sewage

Series 1. Mean temperature 6.3° C.	Series 2. Mean temperature 5.4° C.
5	8
6	9
5	9
7	9
6	9
7	8

*Effect of Sewage* <sup>(1)</sup>

The rate of decomposition of potassium cyanide in solutions containing varying concentrations of sewage is shown in Table 88. No significant change in the rate of decomposition of cyanide is brought about by the addition of sewage. The results of two similar series of experiments in which an effluent from coke oven gas scrubbers was used as the source of cyanide are summarised in Table 89. The initial concentration of effluent was 0.5 per cent. in each case; the only toxic constituent of the effluent in this concentration was the cyanide, which was present in a concentration of approximately 0.04 gm. per 100 litres. As in the case of pure cyanide solutions sewage does not accelerate the rate of decomposition of the effluent.

TABLE 88—*Effect of Sewage on Rate of Decomposition of Solutions of Potassium Cyanide*

Concentration of (CN) : 0·04 gm. per 100 litres

Sewage Per cent.	No. of days to become non-toxic
0	6
0·5	7
0	5
0·5	5
0	4
0·5	5
0	4
0·5	5
0	4
0·5	4
0	3
0·5	6
0·125	4
0·25	6
0·5	5
1	6
0·125	5
0·25	5
0·5	4
1	6
0	5
0·5	7

TABLE 89—*Effect of Sewage on Rate of Decomposition of Cyanides in Effluents from Gas Scrubbers*

Concentration of effluent : 0·5 per cent.

Concentration of sewage Per cent.	No. of days to become non-toxic
0	10
0·25	9
0·5	9
1	7
1·5	9
0	9
0·25	8
0·5	9
1	9
1·5	8

The effect of potassium cyanide on the rate of absorption of dissolved oxygen by sewage, when incubated for 5 days at 18·3° C. in sealed bottles, is given in Table 90. The rate of oxidation of the sewage was reduced to the extent of about 40 per cent. by a concentration of potassium cyanide equivalent to 0·1 gm. (CN)



per 100 litres, and concentrations as low as 0.01 gm. (CN) per 100 litres caused some diminution. This effect is very different from that observed with tar acids.

TABLE 90—*Effect of Potassium Cyanide on Dissolved Oxygen Absorbed from Tap Water by Sewage*

Concentration of (CN)  Parts per 100,000 of the solution incubated	Biochemical oxygen demand of sewage in 5 days at 18.3° C.  Parts per 100,000 (Figures in brackets show percentage reduction due to added potassium cyanide)						Average percentage reduction in B.O.D. of sewage due to (CN)
	Sewage A	Sewage B	Sewage C	Sewage D	Sewage E	Sewage F	
	1 per cent.	1 per cent.	1.5 per cent.	1 per cent.	0.75 per cent.	0.75 per cent.	
0	46.4	9.1	7.5	37.6	56.4	46.8	—
0.01	—	—	7.2 (4)	—	—	—	4
0.02	43.2 (7)	8.6 (5)	7.2 (4)	31.2 (17)	—	—	8
0.03	—	8.1 (11)	6.4 (14)	—	—	—	13
0.04	40.8 (12)	8.0 (12)	4.3 (43)	26.4 (30)	—	—	24
0.05	—	7.4 (19)	—	—	—	—	19
0.06	40.8 (12)	7.3 (20)	3.5 (53)	—	—	—	28
0.07	—	7.0 (23)	—	—	—	—	23
0.08	36.4 (21)	6.7 (27)	—	24.8 (34)	—	—	27
0.09	—	6.9 (25)	—	—	—	—	25
0.10	33.2 (28)	5.1 (44)	—	—	32.0 (43)	25.6 (45)	40

It seemed probable that the reduction brought about by cyanide in the rate of absorption of dissolved oxygen by sewage was due to poisoning of bacteria responsible for the decomposition process. Some experiments were therefore carried out in which dilutions of sewage, with and without the addition of potassium cyanide, were incubated in sealed bottles for 5 days at 18.3° C. and samples were taken daily for bacteriological examination. In Fig. 64 is shown the number of bacteria growing on agar at 20° C. present on each of the 5 days during which the

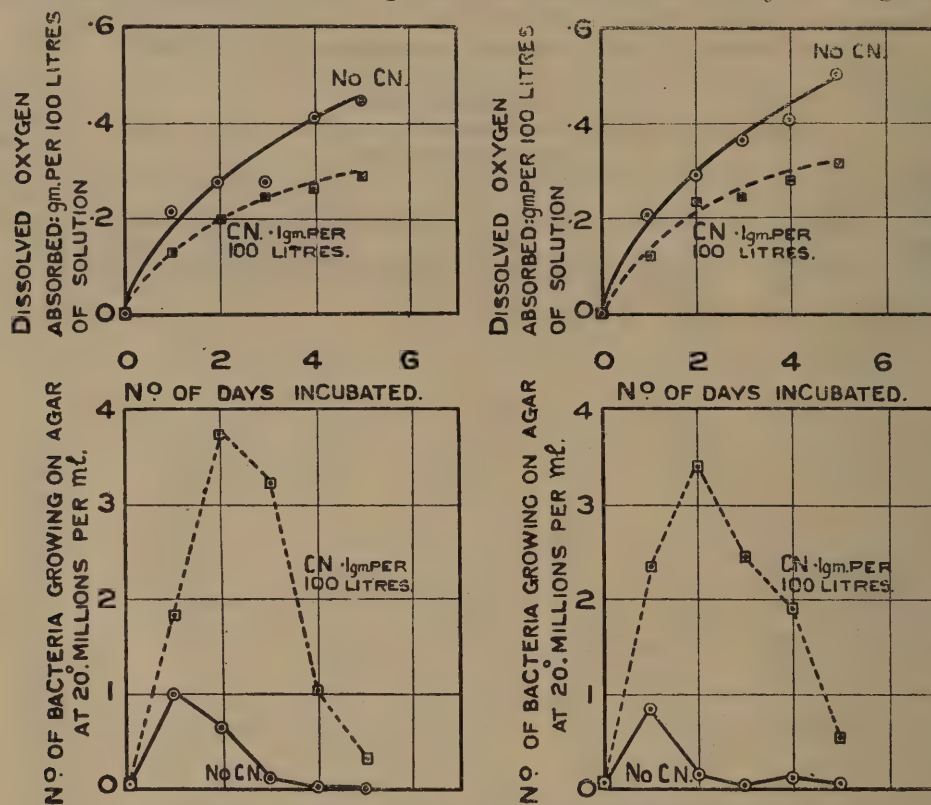


FIG. 64—Effect of Cyanide on the Rate of Absorption of Dissolved Oxygen by Sewage, and on its Bacterial Content

sewage or mixture with cyanide was incubated. The amounts of dissolved oxygen absorbed during the 5 days are also shown. Although the presence of cyanide decreased the amount of dissolved oxygen absorbed, the numbers of bacteria capable of growing on agar at 20° C. were very much greater throughout the 5 days' incubation in the sewage containing cyanide than in the sewage alone. It is possible that particular strains of bacteria were encouraged by the presence of cyanide and that the growth of other strains, active in oxidising sewage, was checked.

#### Effect of Salinity

Data showing the effect of salinity on the rate of decomposition of solutions of pure potassium cyanide and of effluents containing cyanide are summarised in Table 91; the saline solutions were made up with "sea salt." There is no evidence of any significant effect of variations in salinity on the rate of decomposition of cyanide.

#### Decomposition in Estuary Water

In Table 92 figures are given showing the rate of decomposition in Estuary water of pure cyanide and of the cyanide constituent of an effluent from coke oven gas coolers. The rate of decomposition in Estuary water has been compared with the rate of decomposition under similar conditions, but with tap water containing "sea salt" and sewage as the diluent. From the results of this series of experiments it appears that decomposition in Estuary water is more rapid than in tap water containing sewage and salt, and that the rate is particularly high in Estuary water of salinity 15 to 25 gm. per 1000 gm. Some support for this conclusion is provided by the results of an experiment in which a solution of potassium cyanide was diluted with samples of water taken from different parts of the Estuary but adjusted to the same salinity by the addition of "sea salt." The data are summarised in Table 93.



TABLE 91—*Rate of Disappearance of Cyanide in Solutions of Different Salinity*

Concentration of sewage Per cent.	Salinity Gm. per 1,000 gm.	Source and concentration of (CN)	No. of days to become non-toxic
0	0 5 10 15 20 25	KCN 0.04 gm. (CN) per 100 litres	6 5 4 4 4 3
0.5	0 5 10 15 20 25	"	7 5 5 5 4 6
0.5	0 2.3 9.6 14.2 17.5 21.5 22.9	"	6 7 6 6 6 6 7
0	0 5 10 15 20 25	"	4 3 2 2 2 3
0	0 5 10 15 20	"	3 2 3 2 3
0.5	14.4 18.8 22.0 25.1	0.5 per cent. solution of effluent from gas scrubbers	5 5 7 7

TABLE 92—*Rate of Decomposition of Potassium Cyanide diluted with Estuary Water and with Tap Water containing Sewage and "Sea Salt"*

Salinity Gm. per 1,000 gm.	Source and concentration of cyanide	No. of days to become non-toxic	
		Diluent : Estuary water	Diluent : Tap water <i>plus</i> 0.5 per cent. sewage
0 2.3 9.6 14.2 17.5 21.5	KCN equivalent to 0.04 gm. (CN) per 100 litres	6 7 6 4 2 2	6 7 6 6 6 6
14.4 18.8 22.0 25.1	0.5 per cent. solution of coke oven effluent containing cyanide	3 2 2 2	5 5 7 7

TABLE 93—*Rate of Decomposition of Potassium Cyanide Diluted with Estuary Water adjusted to a Salinity Value of 24.9 gm. per 1000 gm.*

Concentration of (CN) : 0.04 gm. per 100 litres

Original salinity of Estuary water	No. of days to become non-toxic
2.3	4
4.3	5
8.4	3
15.5	1
21.6	2
23.8	2
24.9	1

*Effect of Hydrogen Ion Concentration*

The rate of decomposition of solutions of cyanides does not seem to be related to the pH value of the diluent, within the range of hydrogen ion concentration normally found in the Estuary. In two series of experiments pure potassium cyanide was dissolved in tap water with added sewage and adjusted to a salinity of 10 gm. per 1000 gm. with "sea salt." The hydrogen ion concentration of the mixture was varied by the addition of acid or alkali. The rates of decomposition of the cyanide under these conditions are shown in Table 94. There appears to be no consistent difference between the rates of decomposition in solutions of different pH values.

TABLE 94—*Rate of Decomposition of Potassium Cyanide in Mixtures of Tap Water and Sewage of Different Hydrogen Ion Concentrations*

Salinity of mixture : 10 gm. per 1000 gm. Concentration of (CN) : 0.04 gm. per 100 litres

pH	No. of days to become non-toxic
<i>Series 1—</i>	
7.0	4
7.6	4
8.0	4
8.4	5
8.8	5
<i>Series 2—</i>	
7.0	6
7.6	6
8.0	4
8.4	5
8.8	4

From the small amount of information available on the rate of disappearance of cyanides under different conditions, it is impossible to draw any general conclusions as to the mechanism of the decomposition process. When changes in the concentration of a toxic substance are examined by using fish as indicators it is necessary to base any conclusions on many parallel series of experiments, since wide variations occur in the individual resistances of fish. It seems clear, however, that the nature of the decomposition of cyanides is very different from that of phenolic substances, since the great acceleration produced by sewage in the breakdown of *p*-cresol does not occur in the case of cyanides. The evidence collected shows that the decomposition both of pure cyanide and of the cyanide constituent of coke oven effluents is more rapid in Estuary water than in tap water with or without the addition of sewage. This difference, as in the case of tar acids, does not appear to be due either to the presence of sea salts in the estuarine water or to an optimum condition of hydrogen ion concentration. It is possible that the rapid decomposition of both these substances is associated with the presence of a specially active bacterial flora. In the case of cyanide this possibility is



strengthened by the fact that decomposition is more rapid in water taken from the central stretch of the Estuary than in water taken from positions nearer the head of the Estuary, though the acceleration is not due to the difference in salt content.

#### EXTENT OF DILUTION OF INDUSTRIAL EFFLUENTS IN THE ESTUARY

Substances discharged into the Estuary may remain there moving to and fro for some days before passing out to sea. Cyanides and tar acids, the main toxic substances discharged, are during this time partially or completely decomposed. The concentration of these substances in the general body of the Estuary water will thus be lower than the concentration estimated from the weight of toxic substances discharged daily and the volume of new water entering the Estuary every day. Cyanides and tar acids are not evenly distributed throughout the waters of the Estuary. The highest concentrations are, in general, found in the surface layers, and in a stretch of water which varies in length with the tidal range and with other factors. Estimates of the average concentrations in the whole volume of the Estuary water are therefore untrustworthy, but a consideration of the general values found by analysis shows that they are of the order to be expected from the weight of substances discharged and the amount of diluting water available.

The weights of cyanides and tar acids discharged during the spring of 1931, when an intensive survey of the Estuary was carried out, were, very approximately, 1,800 lb. of cyanide (CN) and 4,200 lb. of tar acids per 24 hours. During the 38 consecutive days on which water samples were taken, the mean volume of fresh water entering the Estuary from the upper reaches was approximately 310 million gallons per 24 hours. The volume of new sea water entering the Estuary daily was not directly determined. The ratio of salt to fresh water in the Estuary has, however, been calculated. Under conditions of moderate fresh water flood, such as occurred during the period of the survey, the ratio was approximately 3.5 to 1, so that, as a rough estimate, it may be assumed that the volume of new sea water entering the Estuary daily was about 3.5 times the corresponding volume of fresh water. The total volume of new water available for the dilution of substances discharged into the Estuary would thus be approximately 310 million gallons of fresh and 1,080 million gallons of sea water, making a total of roughly 1,400 million gallons in all. If the cyanide and tar acids discharged had been evenly distributed throughout the whole volume of the Estuary, and if no decomposition had taken place after their discharge, their mean concentration in the Estuary waters during the survey in 1931 would have been 0.013 part (CN) and 0.030 part tar acids per 100,000. The cyanide concentrations actually observed ranged from 0 to 0.035 part (CN) per 100,000, and the mean of 248 determinations was 0.0035. The samples were drawn mostly from the surface waters of the Estuary, where the concentration of cyanide is in general greater than in the deeper layers. Moreover, the area sampled did not include the full length of the Estuary, as the seaward end, where it was found that cyanides were usually absent, was generally omitted. If the cyanide present had been evenly distributed through the whole body of water in the Estuary (with a mean water level 9 ft. above Admiralty datum), the average concentration would have been substantially lower than 0.0035 part per 100,000. As against this some allowance must be made for the fact that the concentration of cyanide as determined by the method available was, in general, lower than the true value. The mean value of tar acids found was 0.016 part per 100,000, this representing the average of 73 determinations in samples taken from the same stretch of the Estuary as the samples from which the cyanide value was obtained. Although it is impossible to compare accurately the calculated and observed concentrations of toxic substances in the Estuary, it will be seen that the mean observed values of cyanides and tar acids were below the calculated values. It is probable that the differences are largely due to the decomposition of the substances after their discharge.

#### REFERENCE

- (1) SOUTHGATE, B. A. *J. Soc. chem. Ind., Lond.*, 1933, 52, 11.



## CHAPTER XVII

FACTORS INFLUENCING BIOCHEMICAL OXYGEN DEMAND OF SEWAGE  
AND OF INDUSTRIAL EFFLUENTS

During the survey, the relative oxygen-absorbing capacities of sewage and of the main industrial effluents discharged into the Estuary were assessed. The most reliable estimate of the effect of such diverse types of material on the concentration of oxygen in the Estuary waters is probably given by a comparison of their biochemical oxygen demands (B.O.D.). In this determination, recommended by the Royal Commission on Sewage Disposal<sup>(1)</sup> and extensively used since that time, an attempt is made to measure the oxygen demand of an effluent under conditions similar to those which arise when it is mixed with the water of a stream. The effluent is diluted with water nearly saturated with dissolved oxygen and incubated in a stoppered bottle for 5 days at 18.3° C. and the weight of oxygen absorbed from solution during this time is determined. In this method the oxidation of organic matter is brought about largely by bacterial activity as under natural conditions in a stream, and in this respect the method is superior to those in which the decomposition is the result of purely chemical oxidation. The rate of oxidation is usually high during the first few days of incubation and thereafter becomes less rapid. In most cases, however, the oxidation of the effluent is not complete at the end of 5 days or even after a considerably longer period. The ratio of the 5-day demand to the total demand varies with different effluents. In the Estuary, the course of the decomposition of effluents after the first few days is unimportant, since substances remaining in solution or suspension will by then have been washed out to sea.

Dilutions of the effluents were incubated in glass bottles, the stoppers of which were tied down. Many varieties of seal for preventing the entry of air into the bottles during incubation have been proposed, and several of these were tried, but the method finally adopted was to immerse the necks of the inverted bottles in vessels of clean tap water. This method was used by Adeney<sup>(12)</sup>, Greenfield and Elder<sup>(8)</sup> and others. Greenfield and Elder concluded that even when the water used for immersing the bottles contained considerable organic matter, in no case was sufficient sealing water sucked into the bottles to cause any appreciable discrepancies in the results.

Data regarding the precision attained in determinations of dissolved oxygen absorbed by sewage effluents were given by the Royal Commission on Sewage Disposal<sup>(3)</sup>. In eight pairs of duplicate determinations the average difference, expressed as a percentage of the mean value for each pair, was 7.3. In results presented by the United States Public Health Department<sup>(9)</sup> the average percentage difference in large numbers of duplicate determinations was of the same order. Hatfield and Morkert<sup>(10)</sup> found a difference of about 5 per cent. under the best conditions. The average percentage difference given by 19 pairs of duplicate determinations of the dissolved oxygen absorbed by sewages and industrial effluents during the Tees survey was 6.5, and the average for the 16 most concordant pairs was 4.6.

In some cases when solutions of effluents, particularly industrial effluents, were incubated and determinations of dissolved oxygen absorbed were made on successive days, the rate of oxidation was found to be irregular. On some occasions the total oxygen absorbed was lower on a given day than on the previous day. This irregularity was not removed by the most careful mixing of the effluent and diluting water. Similar irregularities were reported by the American Public Health Association<sup>(11)</sup>. It is probable that the erratic course of oxidation sometimes observed accounts for the relatively high differences in the amounts of oxygen absorbed by duplicate samples.

In the Tees survey the biochemical oxygen demand of the various effluents was found on successive days up to 5 days. The values were plotted and a smooth curve was drawn through the points so obtained; the B.O.D. on the fifth day was then taken from the curve. It seems probable that this method gives a more accurate result than that obtained by the actual figure after 5 days, without the determination of intermediate values.



## EFFECT OF DILUTION

Data given by the Royal Commission on Sewage Disposal indicated that the B.O.D. of highly diluted sewage effluents decreased with increasing dilution<sup>(4)</sup>. With less diluting water, however, and after the third day of incubation, the rate of oxidation increased with increasing dilution<sup>(5)</sup>. Similar evidence for the decreased oxygen absorption of sewage liquors in high concentrations was given by Adeney<sup>(12)</sup>. The conclusion reached by the United States Public Health Department as a result of the determination of the oxygen absorbed by tannery and strawboard wastes at different dilutions was, however, that the same values were obtained over a wide range of dilutions<sup>(9)</sup>. During the Tees survey it was found that the value of the dissolved oxygen absorbed both by sewage and by industrial effluents was usually higher in dilute than in more concentrated mixtures. The difference was relatively small for weak effluents but was large for strong industrial effluents. Thus, for six samples of industrial effluents the differences in the B.O.D. given in Table 95 were found when concentrations of the effluent of  $\frac{1}{4}$  and  $\frac{1}{2}$  per cent. were incubated at 18.3° C. For 9 samples of a very weak effluent (average B.O.D. 2.2 gm. per 100 litres) the difference between the B.O.D. in 1 in 10 and 1 in 5 dilutions in tap water, expressed as a percentage of the demand in the 1 in 10 dilution, was 9.

TABLE 95—*Biochemical Oxygen Demand of Industrial Effluents Incubated with Estuary Water in Concentrations of 0.25 and 0.5 per cent.*

No. of samples	Average B.O.D. of effluent Gm. per 100 litres		$\frac{A-B}{A} \times 100$
	0.25 per cent. A	0.5 per cent. B	
2	59	54	8
3	168	134	20
1	278	174	37

Usually in determining oxygen absorbing capacity the effluent was incubated at several dilutions, and the B.O.D. at the greatest dilution which caused a reasonable drop in the dissolved oxygen concentration of the mixture was accepted.

## EFFECT OF BACTERIA IN DILUTING WATER

A few experiments were carried out in which coke oven effluents were incubated with water containing sterilising agents; the rate of oxidation under these conditions was inappreciable. Thus the dissolved oxygen absorbed by an effluent from coke oven gas coolers varied between 0 and 0.8 parts per 100,000 in sterilised solutions and between 40 and 50 parts per 100,000 when incubated with Estuary water. It seems clear that the absorption of dissolved oxygen by effluents of this kind is mainly the result of bacterial action. It is important therefore to know to what extent the rate of oxidation is modified by differences in the bacteria in the Estuary water into which the effluents are discharged. An investigation of the distribution of various species of bacteria in the Estuary was not attempted. Some experiments were, however, undertaken to determine the differences in the rate of oxidation of industrial effluents and of crude sewage in water from different parts of the Estuary. The amounts of dissolved oxygen absorbed by crude sewage and by an effluent from coke oven gas coolers when diluted with tap water and with water from the mouth of the Estuary are shown in Table 96. There was a considerable difference between the weight of dissolved oxygen absorbed by the coke oven effluent from tap water and from water taken from the Estuary. The

difference was more strongly marked when a spent still liquor, in which the main oxidisable materials are tar acids, was incubated after dilution with tap water or with estuarine water (Table 97). The variation caused in biochemical oxygen demand by variations in the quality of the diluting water is greater with industrial effluents than with sewage; this is no doubt due to the high bacterial content of sewage which renders the original bacterial content of the diluting water of less importance.

TABLE 96—*Five Day Biochemical Oxygen Demand of Sewage and of an Effluent from Coke Oven Gas Coolers diluted with Tap Water and with Water from the Mouth of the Estuary*

Effluent	No. of samples	Source of diluting water	Average salinity of diluting water	Biochemical oxygen demand, mean value
			Gm. per 1000 gm.	Gm. per 100 litres of effluent.
Crude sewage	6	Tap Water	0	55
		Estuary water	33·3	57
Effluent from coke oven gas coolers.	6	Tap water	0	28
		Estuary water	30·2	46

TABLE 97—*Biochemical Oxygen Demand of a Spent Still Liquor Diluted with Tap Water and with Estuarine Water*

Source of diluting water		Salinity of diluting water	Biochemical oxygen demand
		Gm. per 1000 gm.	Gm. per 100 litres of effluent
Tap .. .. .	.. .. .	0	20
Estuary mouth	.. .. .	33	195
Tap .. .. .	.. .. .	0	26
Tees Bay .. .. .	.. .. .	33	102
Estuary mouth	.. .. .	30	129
Tap ... .. .	.. .. .	0	24
Centre of Estuary	.. .. .	8	170
Tap .. .. .	.. .. .	0	35
Centre of Estuary	.. .. .	10	239

The relation between the biochemical oxygen demand of industrial effluents and the bacterial content of the diluting water was further shown by some experiments in which coke oven effluents, diluted with tap water or with Estuary water, were incubated with and without the addition of sewage. The B.O.D. of the effluent in the presence of sewage was obtained by subtracting the demand of the sewage when incubated alone from that of the sewage and effluent incubated together. The results are given in Table 98. The biochemical oxygen demands of both types of coke oven effluent were increased by the presence of sewage. The increase was greater with spent still liquors than with effluents from gas coolers; the oxidisable material of spent still liquors consists very largely of tar acids, and the accelerating effect of sewage in bringing about their decomposition was previously noted (Chapter XVI). The effect of sewage on the rate of oxidation of both types of effluent was greater with tap water than with Estuary water as diluent. This is no doubt due to the fact that the Estuary water itself contains a rich bacterial flora and the effect of the bacteria contributed by the sewage is thus relatively smaller.



TABLE 98—*Biochemical Oxygen Demand of Industrial Effluents Incubated Alone or Mixed with Sewage*

Description of effluent	Diluting water	Concentration of		Biochemical oxygen demand Gm. per 100 litres of effluent	
		Effluent Per cent.	Sewage Per cent.	Incubated alone	Incubated in presence of sewage
Spent still liquor	Tap water	0.33	0.5	18	135
		0.5	0.5	24	144
		0.33	0.33	36	180
Effluent from gas coolers	Tap water	0.33	0.33	48	60
		1	1	5	11
		1	0.25	10	22
		1	1	11	29
Spent still liquor	Estuary water	0.33	0.5	78	138
Effluent from gas coolers	Estuary water	1	1	32	39
		0.33	0.33	63	132
		0.5	0.5	68	82

The work described has emphasised the dependence of the rate of oxidation of effluents on the bacterial flora of the water in which they are incubated. For the purpose of assessing the effect of effluents when discharged into the Estuary, it was therefore decided to compare their biochemical oxygen demands when diluted with Estuary water. The water of the Tees Estuary contains appreciable amounts of oxidisable material. Before it was used for the dilution of an effluent in the biochemical oxygen demand test it was desirable, therefore, that this material should be largely oxidised without destroying the bacterial flora. With this object a stream of air was bubbled continuously through each sample of Estuary water for a period of about 6 days previous to use. The effect of this treatment is shown by the results, given in Table 99, for portions of a sample of water taken from the middle of the Estuary opposite Cleveland Shipyard.

TABLE 99—*Effect of Aeration on Bacterial Count and Concentration of Oxidisable Material in Water of the Tees Estuary*

Salinity : 4.6 gm. per 1,000 gm.

No. of days aerated	Oxygen consumed from N/80 KMnO <sub>4</sub> in 4 hours at 80° F. Gm. per 100 litres of water	No. of bacteria per ml. of water (grown on agar for 3 days at 18–20° C.)
0	0.335	210,000
2	0.231	130,000
4	0.228	340,000
7	0.119	240,000

## EFFECT OF INORGANIC SALTS

Results have been reported, by various workers, of many experiments on the effect of small concentrations of salts on the biochemical oxygen demand of polluting effluents, but there appear to be relatively few references to work in which the effect of concentrations of salts of the order found in sea water has been studied. Purvis, Macalister and Minnett<sup>(13)</sup> found that sea water had a marked germicidal action on bacteria, and this was confirmed in the case of nitrifying

bacteria by Purvis, McHattie and Fisher<sup>(14)</sup>. Purvis and Coleman<sup>(15)</sup> reported that the organic substances of sewage were but slowly decomposed in sea water and that no nitrites or nitrates were produced as a result of the decomposition. In an investigation conducted by Adeney<sup>(6)</sup> however, it was found that the rate of absorption of dissolved oxygen by sewage proceeded at approximately the same rate in sea water as in fresh water.

During the Tees survey the rate of oxidation of industrial effluents was found to proceed at a considerably higher rate in fresh water than in saline solutions in which the concentration of salts was approximately the same as in sea water. Thus, in a series of mixtures of industrial effluents and sewage the rate of oxidation of the effluent was higher with tap water as the diluent than with tap water containing sodium chloride (Table 100). A similar retarding effect was found when an industrial effluent was incubated with Estuary water to which increasing concentrations of sodium chloride were added (Table 101). An example of the action of "sea salt" in slowing down the decomposition of phenolic substances was also recorded when the decomposition of *p*-cresol in dilute solution was followed by observations of toxicity to trout (Chapter XVI).

TABLE 100—*Biochemical Oxygen Demand of Industrial Effluents Diluted with Tap Water containing Sewage and with Tap Water containing Sodium Chloride and Sewage*

Composition of diluting water	Biochemical oxygen demand : gm. per 100 litres of effluent			
	Effluent from chemical and tar distillation works Incubated for		Effluent from Mond Gas Plant Incubated for	
	2 days	4 days	2 days	4 days
Tap water plus sewage .. .. .	42	74	17	27
Tap water plus sewage plus 34 gm. NaCl per litre.	8	29	0	2

TABLE 101—*Biochemical Oxygen Demand in Five Days of Effluent from Mond Gas Plant Diluted with Estuary Water to which Varying Concentrations of Sodium Chloride were Added*

Salinity of diluting water  Gm. per 1,000 gm.	Biochemical oxygen demand  Gm. per 100 litres of effluent
9.8	42
20.0	30
32.0	23

It appears that the salinity of the Estuary water into which an effluent is discharged may have some influence on the subsequent rate of decomposition of the polluting constituents of the effluent. Owing to the complex hydrographical conditions existing in an estuary, however, the salinity of the water with which a given effluent is mixed during its period of decomposition changes continuously ; no attempt has been made to arrive at an average value for outfalls in the Tees Estuary at different distances from the sea. The water used for the dilution of effluents in the determination of their biochemical oxygen demand was taken from positions in the Estuary in which the salinity was 16–17 gm. per 1,000 gm. ; the salinity was then made up to 17 gm. per 1,000 gm. by the addition of sodium chloride. The influence of varying concentrations of salts on the decomposition of organic material was thus eliminated, and since the water was always taken from about the same relative position in the Estuary, variations in bacterial content were minimised.



## EFFECT OF CONCENTRATION OF DISSOLVED OXYGEN IN DILUTING WATER

It seemed possible that the rate of oxidation of effluents might depend, to some extent, on the level of oxygenation of the water into which they were discharged. If this were so, a true comparison of their relative effect in bringing about the deoxygenation of the Estuary water would not be obtained by the determination of biochemical oxygen demand with well-aerated diluting water. Results obtained by Spitta<sup>(16)</sup>, Theriault<sup>(9)</sup>, the Royal Commission on Sewage Disposal<sup>(7)</sup> and others, indicate, however, that in the biochemical oxidation of polluting effluents, the rate of oxidation is, within wide limits, independent of the initial concentration of dissolved oxygen provided that an excess is always present. This conclusion was confirmed by an experiment in which crude sewage was diluted with tap water containing different quantities of dissolved oxygen and incubated for one day (Table 102).

TABLE 102—*Effect of Concentration of Dissolved Oxygen on Biochemical Oxygen Demand of Sewage*

Original concentration of oxygen	Oxygen absorbed in 1 day at 18.3° C.
Gm. per 100 litres of solution	Gm. per 100 litres of sewage
1.184	30
1.016	30
0.888	32
0.792	33
0.584	33
0.544	29

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## CHAPTER XVIII

## BIOCHEMICAL OXYGEN DEMAND OF SEWAGE AND INDUSTRIAL EFFLUENTS DISCHARGED INTO THE TEES ESTUARY

In the complicated conditions of flow prevailing in an estuary, only a rough estimate can be made of the relative effects of different effluents on the concentration of dissolved oxygen in the estuary waters. The effect of each effluent will depend to some extent on the position of discharge. Effluents discharged into the estuary near the mouth enter a greater volume of water and become mixed with the open waters of the sea after a shorter period than those discharged further upstream. Moreover, the amount of dissolved oxygen absorbed by industrial effluents in a given time depends largely on the chemical and bacteriological condition of the water with which they are diluted, and it seemed probable that this factor might vary considerably in different parts of the Tees Estuary. Estimates of the reduction in the concentration of dissolved oxygen brought about in the Tees Estuary by various types of effluent were based on a comparison of their biochemical oxygen demands under standardised conditions and no attempt was made to estimate the importance of the position of their points of discharge. While the estimates must, for this reason, be approximate, they indicate the relative effects of different discharges, since both industrial and sewage effluents are discharged at points fairly evenly distributed along the central reaches of the Estuary.

Some difficulty arose in making the estimates for industrial effluents, since some were discharged intermittently and others varied considerably in volume from time to time. Data for the volumes of industrial effluents were, in most cases, supplied by the undertakings concerned; they were obtained from measurements of flow over a weir, by estimating the capacity of pumps supplying water for the industrial processes, or by some other convenient method. The composition of many effluents continuously discharged varied considerably from time to time and even greater variations in composition occurred with some effluents intermittently discharged. With such variations it was only possible to make approximate estimates of the weights of oxygen absorbing material entering the Estuary from industrial sources, although the estimates, so far as the more important discharges were concerned, were based on the results of analyses of a number of representative samples.

The sewage from all the main outfalls was discharged into the Estuary at levels between high and low tide marks, and the outlets were fitted with flap valves to prevent the Estuary water entering the sewers. It was not readily possible to measure the flow of sewage directly or to obtain average samples for 24-hour periods, for when the outlet valve was closed by the rising tide, the sewage accumulated in the sewer system immediately before the point of discharge, and stagnant sewage rose in the manhole shafts. It was decided, therefore, to estimate the oxygen absorbing capacity of sewage discharges from an assumed mean value for the biochemical oxygen demand of the sewage per head of population per day and the population served by each sewer.

From published data, particularly those in the Reports of the Royal Commission on Sewage Disposal, it appears that if the quantity of sewage discharged per head of population is from 25 to 30 gallons per day, the 5-day biochemical oxygen demand of a sewage of domestic origin is normally 40 to 60 gm. per 100 litres. The volume of sewage discharged in the Tees-side area, while varying in different districts, was estimated by the local authorities to be about 25 to 30 gallons per head per day. With a flow of 25 gallons per head and a B.O.D. of 60 gm. per 100 litres, the oxygen required in 5 days would be equivalent to 0.15 lb. per head, or with a flow of 30 gallons and a B.O.D. figure of 40, the oxygen required in 5 days would be 0.12 lb. A mean value of 0.135 lb. was taken as the weight of oxygen required in 5 days by the sewage per head of population per day.



## EFFECT OF DEPOSITS OF MUD

The reaches of the Estuary into which the polluting effluents are mainly discharged consist of a dredged channel from which 200,000 to 300,000 cubic yards of material are removed annually by dredging. Over a large part of the length of the Estuary the dredgings consisted of black mud with a high oxygen absorbing capacity (Chapter VI); it was, however, difficult to arrive at an estimate of the total oxygen demand of the mud removed by dredging. Some of the deoxygenating material in the bottom deposits was probably derived from the various effluents discharged into the Estuary.

A few experiments were undertaken to ascertain whether the oxygen absorbed by a deposit of mud bore any relation to the thickness of the deposit. A layer of mud taken from the Estuary foreshore was placed at the bottom of a wide-mouthed glass-stoppered jar completely filled with tap water, and the oxygen absorbed from the water during incubation was determined. The results are given in Table 103,

TABLE 103—*Dissolved Oxygen absorbed from Tap Water during 24 hours, at a Temperature of 65° F., by Mud from the Foreshore of the Tees Estuary opposite Cleveland Shipyard*

Volume of water used in all cases: 800 ml. Area of mud surface: 10 sq. in. The average B.O.D. value of the 3 samples, when small quantities were incubated for 5 days, was 0.0043 gm. oxygen per gm. dry weight of mud,

Weight of wet mud  Gm.	Thickness of layer of mud  In.	Reduction of dissolved oxygen in tap water  Gm. oxygen per 100 litres of water
<i>Sample 1</i> 169 169 118	1.12 0.75 0.62	0.20 0.17 0.18
<i>Sample 2</i> 137 117 78 51 41	1.25 1.06 0.75 0.56 0.44	0.18 0.17 0.11 0.18 0.20
<i>Sample 3</i> 89 49 32	0.81 0.50 0.37	0.12 0.10 0.08

The amount of oxygen absorbed did not vary appreciably with different depths and weights of mud of the same total surface area. It would seem therefore that only the surface layer of the material which settles to the bottom of the Estuary is active in absorbing oxygen from the water above it, and that the mud below the surface remains in a deoxygenated condition until it is dredged and deposited in the sea. A similar conclusion was reached by Mohlman and his colleagues, working on the Illinois River<sup>(1)</sup>. The mud deposits between Stockton and Cargo Fleet absorb, on the average, about 0.0035 gm. of oxygen per gm. dry weight of mud, when incubated for 5 days at 18.3° C. (Fig. 19). The mean 5-day B.O.D. of the mud referred to in Table 103 was 0.0043 gm. per gm. dry weight, and this mud, when incubated for 1 day, absorbed an average of 0.15 gm. oxygen per 10 sq. in. of surface. The corresponding oxygen demand in 5 days may be taken, very roughly, as 0.3 gm. per 10 sq. in. The mean 5-day oxygen demand for the mud between Stockton and Cargo Fleet may therefore be estimated to be of the order of 0.2–0.3 gm. oxygen per 10 sq. in. of mud surface, or 3.0–4.0 gm. per sq. ft.

The length of the muddy section of the Estuary is about 30,000 ft., and the average width of the mud deposits about 300 ft. The mud is not continuous throughout the whole section but it probably covers at least a third of the total area, that is, 3 million sq. ft. The dissolved oxygen absorbed in 5 days at 18·3° C. by the mud deposits, calculated on this basis, would then be of the order of 10,000 kg. (22,000 lb.) or the equivalent of the 5-day B.O.D. of domestic sewage from 160,000 persons per day. The total population from which sewage is discharged into the Estuary is about 280,000. This estimate of the oxygen absorbing capacity of the mud deposits must be regarded only as giving the order of their importance. It is interesting to note that it has recently been found that on the Illinois River<sup>(1)</sup> the oxygen absorbing capacity of the mud deposits is greater than that of the raw sewage daily discharged, and the concentration of oxygen in the Illinois River is largely dependent on the extent to which the bottom deposits are stirred up by the action of the river current.

The extent to which industrial effluents and sewage contribute to the bottom deposits is not known. Some determinations of the oxygen absorbed from acid permanganate by different types of polluting material before and after filtration were, however, carried out (Table 104). The proportion of the oxidisable material in solution was greater in all cases in the industrial effluents examined than in raw sewage. The oxidisable material of effluents Nos. 11, 14 and 154 consisted largely of soluble tar acids, the preponderating influence of which in raising the oxygen demand of effluents has been pointed out elsewhere<sup>(2)</sup>.

TABLE 104—Oxygen Consumed from N/8 Potassium Permanganate in 4 Hours at 80° F. by Industrial Effluents and Sewage before and after Filtration

Effluent	No. of samples	Oxygen absorbed Gm. per 100 litres		Ratio : $\frac{\text{Filtered effluent}}{\text{Unfiltered effluent}}$
		Before filtration	After filtration	
Crude sewage	4	41·3	18·4	0·42
Effluents from coke oven gas coolers (Nos. 31 & 59)	5	82·3	55·5	0·67
Effluent from chemical and tar distillation works (No. 11)	2	298	283	0·95
Effluent from Mond Gas Plant (No. 14)	1	105	91	0·87
Spent still liquor (No. 154)	1	336	335	1·00

SEWAGE

Untreated sewage is discharged from 49 main outfalls belonging to local authorities, and there are, in addition, 27 discharges of sewage from industrial works on the banks of the Estuary (Table 36). While the population served by the municipal outfalls has been ascertained, no information has been collected on the relative importance of the industrial sewers. The majority of the employees of the industrial works on the Estuary banks live in the Tees-side area and have already been included in the population served by the town sewers.

The sewage discharged from the outfalls belonging to the local authorities is almost entirely of domestic origin. The contributing population (estimated from figures supplied by the Borough Engineers) and the estimated 5-day B.O.D. of the sewage, using the figure of 0·135 lb. as the 5-day B.O.D. per head, are shown in Table 105.



TABLE 105—*Five-Day Biochemical Oxygen Demand of Domestic Sewage discharged into the Estuary*

Authority	Population	Approximate total 5-day B.O.D. of the sewage discharged per 24 hours  Oxygen in lb.	Percentage of total B.O.D. of sewage discharged
Billingham U.D.C.    ..    ..	17,690	2,400	6
Eston U.D.C.    ..    ..    ..	30,950	4,200	11
Middlesbrough Corporation    ..	138,500	18,700	49
Stockton R.D.C.    ..    ..    ..	1,580	200	1
Stockton U.D.C.    ..    ..    ..	68,000	9,200	24
Stokesley R.D.C.    ..    ..    ..	420	60	—
Thornaby Corporation    ..    ..	23,660	3,200	8
Total    ..    ..	280,800	37,960	—

TABLE 106—*Five-day Biochemical Oxygen Demand of Industrial Effluents discharged into the Estuary*

Effluent No.	Source of effluent	No. of samples examined	5-day B.O.D.  Parts per 100,000	Approx. flow  Gal. per 24 hours	5-day B.O.D. of effluent discharged per 24 hrs.  Oxygen in lb.
10	Coke oven gas coolers    ..    ..	2	77	630,000	4,850
11	Chemical and tar distillation works	5	223	23,000	510
14	Mond Gas Plant    ..    ..	3	50	48,000	240
31	Coke oven gas coolers    ..    ..	7	61	1,080,000	6,600
35	Producer gas seals    ..    ..	1	7	180,000	126
59	Coke oven gas coolers    ..    ..	1	65	1,080,000	7,020
83	Grain washings    ..    ..    ..	1	70	38,400	270
128	Gas works effluent    ..    ..	1	150	1,100	16
137	Chemical works    ..    .. (Cooling, gas washing, etc.)	9	1.6	30,800,000	*4,580
138	Chemical works    ..    .. (Cooling, gas washing, etc.)	2	0.5	66,000,000	*3,300
155	Effluent from tar works    ..	4	30	24,000	72
159	Spent still liquor    ..    .. (Coke oven plant)	5	217	36,500	790
	TOTAL				28,374

\* Effluent No. 137 includes the sewage from about 5,200 workmen. The 5-day B.O.D. value of this sewage, estimated at 350 lb. per 24 hours, has not been included in the figure given. In Effluents Nos. 137 and 138, the B.O.D. value is the difference between that of the ingoing and outgoing Estuary water.

## INDUSTRIAL EFFLUENTS

The biochemical oxygen demand of industrial effluents, other than spent pickle liquors, was determined by diluting the samples with aerated Estuary water of salinity approximately 17 gm. per 1,000 gm. and incubating for 5 days at 18.3° C. Some of these effluents are subject to considerable variations in composition and volume, and the figures given in Table 106 are necessarily rough approximations.

The oxygen demand of spent pickle liquors was calculated from the weight of ferrous iron discharged daily. The output of this type of effluent may vary considerably with fluctuations in the demand for galvanised steel; in 1932 several of the works were closed or were working below full capacity. The figures given for the volume of effluent discharged were supplied by the manufacturers concerned and are representative of normal conditions.

In some works the acid solution of ferrous chloride or sulphate is neutralised with lime before being discharged, and it is probable that partial oxidation of the ferrous iron then takes place before it reaches the Estuary. Oxidation is further assisted in some works where the effluent is stored in tanks and discharged at a steady rate into the Estuary. The calculated oxygen demand of spent pickle liquors (Table 107) is thus probably rather greater than the true value, but the figures should be of the right order.

TABLE 107—*Calculated Oxygen Demand of Spent Pickle Liquors discharged into the Estuary*

Effluent No.	Weight of ferrous iron discharged	Oxygen demand
	Lb. per 24 hours	Lb. per 24 hours
5	2,860	409
46	2,090	299
49	1,740	249
53	73	10
123, 124, 125	8,370	1,196
Total	15,133	2,163

Whereas the oxidation of sewage and of industrial effluents of the coke oven type proceeds relatively slowly, ferrous iron is oxidised rapidly in the alkaline waters of the Estuary, so that the whole oxygen demand of effluents from galvanising works will be exerted before they are carried out to sea.

In addition to their action in absorbing oxygen, effluents containing oxidisable material, if discharged in a de-aerated condition, may cause an immediate fall in the concentration of dissolved oxygen in the Estuary water; this effect, however, must be relatively small. Thus, if sewage were saturated with dissolved air, it would contain only about 1 part of oxygen per 100,000, whereas the weight of oxygen absorbed by the decomposition of the oxidisable matter in 5 days is about 50 parts per 100,000. The difference is even greater with coke oven effluents, which normally have much higher oxygen demands. In the winter, the sewage discharged into the Estuary was comparatively well oxygenated. For example, samples from two sewers, taken from manholes immediately before the point of discharge, had, respectively, oxygen concentrations of 59 per cent. of saturation at 7.5° C. and 61 per cent. at 7° C. These sewers were comparatively short and served two districts on the south side of the Estuary. In warmer weather the concentration of dissolved oxygen in the sewage would be less.

Some loss of dissolved oxygen may also result from the circulation of Estuary water through the condensers of certain works. Normally the water is heated but is not polluted during the circulation. In comparison with the oxygen demand of effluents, the loss of dissolved oxygen in water used for cooling condensers must be relatively small.



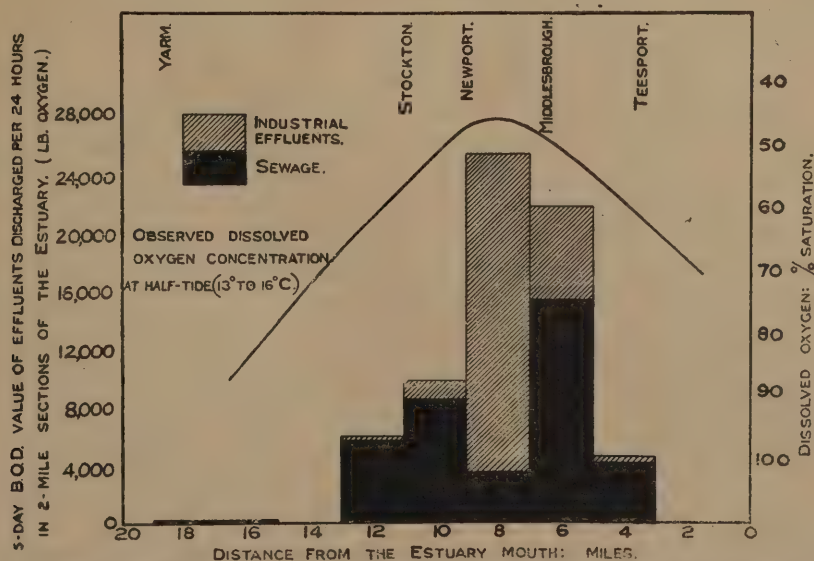
## RELATIVE OXYGEN DEMAND OF SEWAGE AND INDUSTRIAL EFFLUENTS

Disregarding the effect of sedimentation on the oxygen demand of the different types of effluent and also the probably small effect of the initial partial deoxygenation of some discharges, Table 108 shows the estimated total relative oxygen demands of the main types of effluent. Whilst the total volume of domestic sewage discharged has been estimated from figures for the population served, only the main industrial outfalls have been examined. Such discharges as those classed as "land drains" (Table 36) probably contain some oxidisable material arising from industrial processes. Industrial effluents are therefore probably responsible for a slightly larger fraction of the total oxygen demand than that given in Table 108. The figures should not, however, be seriously affected by the inclusion of the small unexamined discharges.

TABLE 108—*Relative Oxygen Demand of the Main Types of Effluent discharged into the Estuary*

Type of effluent	Estimated 5-day B.O.D. of effluent discharged per 24 hours  Oxygen in lb.	Percentage of total B.O.D. of effluents discharged in 24 hours
Domestic sewage .. .. .	37,960	56
Effluents from coke oven gas coolers ..	18,470	27
Spent still liquor .. .. .	790	1
Other industrial effluents, excluding spent pickle liquors	9,110	13
Spent pickle liquors .. .. .	2,160	3
Total .. .. .	68,490	100

In Fig. 65 the oxygen demands of sewage and industrial effluents discharged in different sections of the Estuary are shown. The bulk of the oxidisable material is discharged between Stockton and Teesport, the most heavily polluted region lying between Newport and Middlesbrough. A curve is included to show the average observed dissolved oxygen concentration in the Estuary at half-tide and at a temperature of 13° to 16° C.; this curve has been drawn from data discussed in Chapter IV. The minimum values for dissolved oxygen occur in the reaches

FIG. 65—*Oxygen Demand of the Effluents discharged into the Tees Estuary*

receiving the greatest quantities of oxidisable material. The deoxygenating effect of sewage and industrial effluents extends, however, for a considerable distance on both sides of the position at which they are discharged, since, under tidal action, the Estuary waters move to and fro past the outfalls.

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## CHAPTER XIX

REMOVAL OF CYANIDES FROM COKE OVEN EFFLUENTS<sup>(1)</sup>

For some years considerable attention has been given to problems of treatment and disposal of effluents from coal carbonisation industries. A review of the literature of the subject was published in 1927 by the Liquor Effluents Research Committee of the Institution of Gas Engineers, and since then the gas industry has carried out much experimental work with the objects of reducing the quantity and the polluting character of the effluents and of improving the methods of disposal<sup>(2)</sup>; in addition, many similar investigations have been undertaken abroad, particularly in Germany and America.

Most of this work has been directed towards the problem of treatment and disposal of effluents from gas and coke works employing the indirect process of ammonia recovery. In this process about 85 per cent. by volume of the effluent consists of spent liquor from the ammonia still, and about 15 per cent. of "devil liquor" from the heat exchangers and coolers which follow the saturator in which the ammonia is converted into ammonium sulphate. The main constituents of still effluent and "devil liquor" are monohydric phenols, higher tar acids, sulphides, thiocyanates and thiosulphates.

The methods which have been proposed for facilitating the disposal of gas works effluents are of three main types:—

- (1) Methods designed to reduce the volume of spent liquor produced.
- (2) Methods designed to modify its composition.
- (3) Methods of purification or disposal of the spent liquor.

In general, the methods proposed for the reduction of the volume of effluent produced depend on a reduction in the volume of water used in washing ammonia from the coal gas. Modifications of gas works practice designed to improve the quality of the effluent consist mainly of measures to minimise the oxidation of sulphides and cyanides to thiocyanates, which have a high deoxygenating effect, and of modifications in the methods of removal of tar and liquor from the gas so as to reduce the quantity of tar acids dissolved by the liquor. Methods of treatment proposed include the biological oxidation of the effluent on percolating filters with or without the addition of sewage, chemical oxidation by air, ozone and hypochlorites, and evaporation by coke quenching, injection into a hot chimney, or some similar method. Methods designed to remove only phenolic bodies include simple boiling, volatilisation of phenol by hot flue gases, and extraction with solvents or absorbents.

It has been shown that, in the Tees Estuary, the most poisonous type of industrial waste discharged consists of effluents containing cyanide which result from the cooling of coke oven gas by direct contact with water after ammonia has been recovered by either the direct or semi-direct process (see Chapter XII). The discharge of such effluent could be avoided by the adoption of an indirect system of cooling, and this process is, in fact, in use in certain installations on Tees-side. If direct contact with cooling water were retained, a closed circuit might be employed, the hot effluent from the gas scrubbers being cooled and re-circulated. In a system of this kind it would probably be necessary to draw off a proportion of the effluent cooling water at intervals, disposing of it by use in coke quenching or by other means, and to make up the volume with fresh water, in order to keep down the concentration of dissolved substances.

After the experiments during the 1931 smolt migration had shown that cyanide was the main toxic factor responsible for the death of fish in the Tees Estuary, it was suggested that it might be possible to devise a method by which cyanides could be removed from effluents over a short experimental period without involving any large structural alterations to existing plant. It was hoped, if a successful method were found, to observe the changes brought about in the toxicity of the Estuary waters by the cessation of cyanide discharge. Among the methods which might be used over short periods for the destruction of cyanides in effluents the following were considered: treatment with formaldehyde, conversion to sulphonyl cyanide, oxidation to cyanate and conversion to ferrocyanide.

Formaldehyde reacts with cyanide to form cyanhydrin,  $\text{CH}_2(\text{OH})\text{CN}$ . This reaction is reversible<sup>(3)</sup> and an excess of formaldehyde would probably be required for complete conversion of the cyanide. As formaldehyde is expensive, it was decided not to proceed with experiments to determine the minimum quantity of formaldehyde necessary for conversion of cyanide in the concentration in which

it occurs in coke oven effluents. In the laboratory experiments described in Chapter XIV a very large excess, about 150 times the theoretical amount, was used.

Of the other methods considered, treatment with ferrous chloride to convert the cyanide into ferrocyanide was of special interest in that concentrated solutions of ferrous chloride are produced as a waste product in the “pickling” of steel before galvanising (Chapter XII), and are discharged into the water of the Tees Estuary in which they are oxidised by the dissolved oxygen. The ferrous chloride could thus be obtained locally for the cost of transport from the galvanising works to the coke works. It appeared that the cost of materials for treatment by any of the other processes considered would be very much higher than the cost of conversion to ferrocyanide, and a preliminary investigation of this process was accordingly begun.

CONVERSION OF CYANIDE TO FERROCYANIDE BY TREATMENT WITH FERROUS CHLORIDE

In a preliminary series of experiments it was found that pure solutions of cyanide, in concentrations of the order occurring in coke oven effluents, could be converted into ferrocyanide by the addition of ferrous chloride. Part of the ferrous chloride was oxidised by the dissolved oxygen of the solution and it was necessary to add an excess sufficient to allow for this loss; in air-free solutions cyanide was converted to ferrocyanide almost quantitatively.

The effluents to be treated consisted of Estuary water which had been used to cool coke oven gas by direct contact. Analyses of typical samples are given in Table 37. In treating these effluents it was found that their content of hydrogen sulphide, the concentration of which usually varied from 2 to 20 parts per 100,000, interfered considerably with the conversion of cyanide to ferrocyanide. Part of the ferrous chloride added was immediately precipitated as ferrous sulphide, which then reacted with the cyanide, though much more slowly than did soluble ferrous chloride. In addition, free acid was produced as a result of the reaction :  $\text{FeCl}_2 + \text{H}_2\text{S} \rightarrow \text{FeS} + 2\text{HCl}$ ; unless this was neutralised, the rate of conversion of cyanide to ferrocyanide was considerably reduced. The precipitate of ferrous sulphide rapidly settled out, and, in order that the reaction between ferrous sulphide and cyanide might proceed, it was necessary to stir the effluent continuously during treatment. The rate of reaction of cyanide with ferrous chloride increased with temperature. The laboratory experiments were carried out at 20° C., which was approximately the temperature of the effluents immediately before their discharge into the Estuary. A volume of ten litres of effluent was used in each experiment.

With effluents containing hydrogen sulphide, the rate of disappearance of cyanide by treatment with ferrous chloride alone was slow, and the time required increased with an increase in the concentration of hydrogen sulphide. The time of treatment may be decreased by the addition of excess ferrous chloride. Table 109 shows the rate of purification of typical samples of effluent No. 59, which contained relatively small concentrations of hydrogen sulphide (2·9 to 3·2 parts per 100,000).

TABLE 109—*Treatment of Effluent from Coke Oven Gas Coolers with Different Concentrations of Ferrous Chloride*

Duration of Treatment  Hours	Time taken by trout to overturn in a 1 per cent. solution of treated effluent				
	12 gm. FeCl <sub>2</sub> per 100,000 ml. of effluent			24 gm. FeCl <sub>2</sub> per 100,000 ml. of effluent	
	Sample No. 1	Sample No. 2	Sample No. 3	Sample No. 1	Sample No. 2
1	13 min.	9 min.	10 min.	5 min.	10 min.
2	5 min.	9 min.	18 min.	16 min.	11 min.
4	1½ hours	21 min.	2 hours	47 min.	1½ hours
5	17½ hours	1½ hours	1 hour	> 17 hours	< 17½ hours
6	Non-toxic	< 16½ hours	Non-toxic	Non-toxic	> 17½ hours



It appeared from these and similar experiments that cyanide could be completely or almost completely removed by adding 12 to 24 parts of ferrous chloride to 100,000 parts of effluent (about 1 cwt. pickle liquor containing 40 per cent. of ferrous chloride to 35,000 to 70,000 gallons of effluent), and allowing a period of contact of about 7 hours. For two of the three effluents to be treated (Nos. 59 and 31) a seven hours' flow would in each case amount to 250,000 to 380,000 gallons. To minimise the inconvenience of storing and agitating such large volumes, attention was turned to the conditions under which the period of reaction could be decreased by the use of both ferrous chloride and lime.

A typical series of results showing the effect of increasing concentrations of ferrous chloride and lime on the rate of cyanide removal is shown in Table 110, which refers to the treatment of an effluent containing 10·4 gm. hydrogen sulphide and 7·1 gm. cyanide per 100,000 ml.

TABLE 110—*Treatment of Effluent from Coke Oven Gas Coolers with Ferrous Chloride and Lime*

CaO added  Gm. per 100,000 ml. of effluent	FeCl <sub>2</sub> added  Excess over theoretical amount  Per cent.	Time taken by trout to overturn in 1 per cent. solution of treated effluent			
		Duration of treatment of effluent			
		Hours			
		1	2	3	4
0	100	4 min.	6 min.	11 min.	>1½ hours
	200	3 min.	7 min.	70 min.	Non-toxic
15	100	10 min.	14 min.	36 min.	17 hours
	200	22 min.	Non-toxic	Non-toxic	Non-toxic
20	100	35 min.	>1½ hours	Non-toxic	Non-toxic
	200	2 hours	Non-toxic	Non-toxic	Non-toxic

The rate of purification was increased by increasing the concentration either of ferrous chloride or of lime. The actual length of the reaction period again depended on the hydrogen sulphide content of the effluent ; the effect of increasing hydrogen sulphide concentration on the rate of cyanide removal is illustrated in Table 111, which shows the reaction time necessary to render a series of samples containing different concentrations of hydrogen sulphide innocuous in 1 per cent. solution. From these figures it appeared that it should be possible to treat successfully a gas-washing effluent by mixing with it for ¼ hour 30 parts of CaO and 13 parts of FeCl<sub>2</sub> per 100,000, provided the hydrogen sulphide content did not exceed about 4 parts per 100,000.

In the course of these experiments, the necessity for continuous and complete agitation of the effluent during treatment was emphasised. It was thought that it might be of advantage to mix the lime and pickle liquor before their addition to the effluent and a few experiments were carried out to examine this point. In Table 112 is shown the relative purification of an effluent brought about by mixing with it for 15 minutes lime and pickle liquor added separately and lime and pickled liquor mixed together and stirred before being added. Less cyanide was removed from the effluent when the reagents were mixed before addition than when they were added separately. This is presumably due to the oxidation to ferric hydroxide of the ferrous hydroxide formed in a mixture of ferrous chloride and lime. Even less purification of the effluent occurred when the lime and ferrous chloride were mixed and aerated before being added.

TABLE 111—*Treatment of Effluent from Coke Oven Gas Coolers with Ferrous Chloride and Lime*

Composition of effluent Gm. per 100,000 ml.		Time of treatment necessary to render a 1 per cent. solution of effluent innocuous to trout (hours)			
Alkalinity as CaO	Hydrogen Sulphide	13 gm. FeCl <sub>2</sub> 15 gm. CaO per 100,000 ml. of effluent	13 gm. FeCl <sub>2</sub> 30 gm. CaO per 100,000 ml. of effluent	19 gm. FeCl <sub>2</sub> 15 gm. CaO per 100,000 ml. of effluent	19 gm. FeCl <sub>2</sub> 30 gm. CaO per 100,000 ml. of effluent
1·7	0·5	—	—	—	$\frac{1}{4}$
6·7	3·2	—	—	—	$\frac{1}{4}$
8·4	3·3	$1\frac{1}{4}$	$\frac{1}{4}$	$1\frac{1}{4}$	$\frac{1}{4}$
7·8	3·6	$2\frac{1}{4}$	$1\frac{1}{4}$	$2\frac{1}{4}$	$\frac{1}{4}$
9·0	3·7	—	$\frac{1}{4}$	—	—
6·7	4·3	$2\frac{1}{4}$	$\frac{1}{4}$	$2\frac{1}{4}$	$\frac{1}{4}$
9·5	4·9	$2\frac{1}{4}$	$1\frac{1}{4}$	—	—
10·2	6·6	$>2\frac{1}{4}$	—	—	—
9·8	8·9	$>4\frac{1}{4}$	$4\frac{1}{4}$	$3\frac{1}{4}$	$2\frac{1}{4}$
14·0	9·7	—	—	$3\frac{1}{4}$	$1\frac{1}{4}$
14·6	10·0	—	$>2\frac{1}{4}$	—	$1\frac{1}{4}$
16·8	10·4	$>4\frac{1}{4}$	$3\frac{1}{4}$	$2\frac{1}{4}$	$2\frac{1}{4}$
27·4	19·9	—	$3\frac{1}{4}$	—	—

TABLE 112—*Treatment of Effluent from Coke Oven Gas Coolers with Ferrous Chloride and Lime added Together and Separately*

Concentration of CaO and FeCl <sub>2</sub>  Parts per 100,000	Time taken by trout to overturn in 1 per cent. solution of treated effluent	
	(a) CaO and FeCl <sub>2</sub> added separately	(b) CaO and FeCl <sub>2</sub> mixed before addition
12 CaO .. .. . 19 FeCl <sub>2</sub> .. .. .	50 min.	$9\frac{1}{2}$ min.
30 CaO .. .. . 19 FeCl <sub>2</sub> .. .. .		
	Non-toxic	3 hours

In most of the experiments the effluent was stirred mechanically, but in a few cases the precipitate of ferrous sulphide was kept in suspension by a continuous stream of air. It was found that the stream of air increased the rate of disappearance of cyanide to a greater extent than could be accounted for by its purely mechanical effect. In some cases aeration of an effluent for about 4 hours at 30° C. removed the cyanide without the addition of any ferrous chloride. It is possible that under these conditions the cyanide is volatilised or that the hydrogen sulphide present is oxidised, giving free sulphur which reacts with the cyanide to form sulphocyanide. No diminution in the toxicity of an untreated effluent was brought about by mechanical agitation at 30° C.

By the courtesy of Messrs. Dorman Long & Co., Ltd., a series of large scale tests of the treatment of coke oven effluent with spent pickle liquor was carried out at the Newport Ironworks. The effluent from the gas scrubbers ordinarily passed through two settling tanks, fitted with baffles and arranged in parallel, where it deposited naphthalene and some light oil before being discharged into the Estuary. During the tests the main bulk of the effluent was allowed to pass



through one of these tanks, the fraction to be treated being diverted to the second tank, in which the flow was regulated by a valve and measured by a V-notch at the outlet. A suspension of lime was run into this tank from a mixing vessel, the contents of which were agitated by compressed air. Effluent from the outlet of the tank was pumped continuously into the lime-mixing vessel, slaked lime being added intermittently by hand. Pickle liquor was run in from an inverted carboy, the flow being measured and regulated from time to time. The contents of the tank were mixed continuously by hand and some additional mixing was provided by a pump which circulated effluent from one end of the tank to the other. Approximately 80 gallons of effluent per minute were treated, this representing about one-tenth of the total supply. The amount of lime added was 3 lb. per 1,000 gallons (30 parts per 100,000), and of pickle liquor (containing 40 per cent.  $\text{FeCl}_2$  and of specific gravity 1.38) 0.025 per cent. by volume (13.8 parts  $\text{FeCl}_2$  per 100,000). A period of contact of about one hour was given, the capacity of the lime mixer and design of the settling tanks making it impossible to experiment with shorter periods. Samples of outflowing treated liquor were taken at hourly intervals and the toxicity of 1 per cent. solutions to trout was compared with the toxicity of the inflowing liquor. When conditions had become steady, the treated effluent in 1 per cent. solutions was found to be innocuous to trout over periods of 24 hours; corresponding solutions of the untreated effluent were toxic in a few minutes.

#### REMOVAL OF CYANIDE FROM COKE OVEN EFFLUENTS BY SPRAYING

In some preliminary experiments small quantities of effluent (No. 59) were sprayed from a small medical atomising apparatus standing in a water bath at a constant temperature. The effluent was ejected once only in the form of a fine mist impinging on the walls of an open-mouthed collecting vessel. The original cyanide content of the effluent was 4.1 gm. (CN) per 100,000 ml. The diminution in toxicity brought about by atomisation at different temperatures is shown in Table 113.

TABLE 113—*Treatment of Effluent from Coke Oven Gas Coolers by Spraying at Various Temperatures*

Temperature of effluent before spraying °C.	Time taken by trout to overturn in a 1 per cent. solution of sprayed effluent (Untreated effluent : 11 min.)	
	Hours	Minutes
10	—	24
20	1	45
30	2	22
40	4	13
60	Non-toxic	

Experiments on a larger scale were then undertaken. About 10 litres of effluent were heated to the required temperature and transferred to a 20-litre carboy, fitted with a delivery tube dipping nearly to the bottom and with a second tube passing just through the stopper and connected to a pump with a non-return valve. After compressing the air above the effluent, the latter was allowed to escape through the delivery tube as a jet, which impinged on a spherical metal baffle to form a fine spray. The reduction in the cyanide content depended largely on the efficiency of the atomising apparatus. With the most efficient type of spraying achieved in this series of experiments, the results given in Table 114 were obtained. The original cyanide concentration was 3.3 gm. (CN) per 100,000 ml.

TABLE 114—*Treatment of Effluent from Coke Oven Gas Coolers by Spraying at Various Temperatures*

Temperature of effluent before spraying °C.	Time taken by trout to overturn in 1 per cent. solution of sprayed effluent	
	Hours	Minutes
40	1	21
50	21	0
60	Non-toxic	

A test of the process on a large scale was then carried out at the Newport Ironworks, where facilities were provided by the courtesy of Messrs. Dorman Long & Co., Ltd. The flow of coke oven effluent through one of the naphthalene settling tanks was stopped and the effluent in this tank was heated by steam. A small rotary pump was used to spray the heated effluent through an atomiser of the type used in the direct cooling towers of the ammonia recovery plant. The degree of atomisation achieved by this means appeared to be considerably less than that produced by the laboratory apparatus used in the experiments reported in Table 114. The reduction in the toxicity of the effluent brought about by spraying at different temperatures is shown in Table 115. The original concentration of cyanide varied from 2·2 to 3·0 gm. (CN) per 100,000 ml.

TABLE 115—*Results of Large Scale Test of Treatment of Effluent from Coke Oven Gas Coolers by Spraying*

Temperature of effluent before spraying °C.	Time taken by trout to overturn in a 1 per cent. solution of sprayed effluent Min.
23	7
28	16
35	15
41	14
47	17
50	40
53	48
58·5	115

It was, for various reasons, found impossible, during the period of the survey, to apply any of the methods of reducing the quantity of cyanide entering the Estuary. There was thus no opportunity of observing the effects of the methods suggested in reducing the toxicity of the Estuary waters and so in reducing the mortality of smolts.

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## APPENDIX

## I. NOTES ON METHODS OF ANALYSIS

The *salinity* of water from the Tees Estuary was determined by titration of 10 ml. with a standard solution of silver nitrate containing 27.25 gm. per litre, using potassium chromate as indicator. The solution of silver nitrate was standardised against Standard Sea Water\* and the titration values for the samples of Estuary water were converted to salinity with the aid of Knudsen's Hydrographical Tables<sup>(1)</sup>. Without any special precautions the method gives salinity to within 0.1 gm. per 1,000 gm.

*Dissolved oxygen, nitrite, free and saline ammonia, and albuminoid ammonia* were determined by the following methods described in the Ministry of Health's publication on "Methods of Chemical Analysis as applied to Sewage and Sewage Effluents"<sup>(2)</sup>: dissolved oxygen by Winkler's method, usually as modified by Rideal and Stewart; nitrite by the Griess-Ilosva method; free and saline ammonia by distillation and Nessler's reagent; albuminoid ammonia, after removal of free and saline ammonia, by distillation with alkaline permanganate of potash and addition of Nessler's reagent to the distillate.

*Total nitrogen* in samples of mud was determined by the Kjeldahl method.

*Phosphate* in samples of Estuary water was determined by the method of Denigès,<sup>(3)</sup> using solutions of ammonium molybdate and of stannous chloride.

*pH values* of samples of water were determined colorimetrically and the necessary corrections were made for the effects of salts in solution.

*Ferric iron* in samples of water was determined colorimetrically by the use of a standard thiocyanate solution.

*Tar acids* in samples of industrial effluents and of Estuary water were determined by steam distillation and estimation of the concentration of tar acids in the distillate by the method of Fox and Gauge<sup>(4)</sup>. This method depends on the production of coloured compounds when tar acids are treated with diazotised sulphanilic acid. The colour given by different phenolic bodies varies considerably, and the most satisfactory standard for use with Tees Estuary water was found to be the mixture of tar acids contained in the fraction of creosote oil distilling between 205° and 230° C. In standardising this fraction the tar acids were extracted with caustic soda and were estimated by bromination<sup>(5)</sup>. The method of Fox and Gauge is not entirely specific for tar acids of industrial origin, since peaty material and other plant products give a similar reaction. The errors arising from this source in the estimation of tar acids in samples of Estuary water were, however, negligible.

*Cyanide* was determined by a modification of Weehuizen's<sup>(6)</sup> method, using phenol phthalin, by Liebig's method<sup>(7)</sup>, using silver nitrate, or by conversion to Prussian blue, according to the concentration of cyanide in the sample under examination.

By the modification of Weehuizen's method, the sample (200 ml.) is acidified with 0.5 gm. of tartaric acid and distilled. To the distillate (50 ml., collected in a Nessler tube containing 4 ml. of 2 per cent. caustic soda solution) are added 0.25 ml. of a solution of phenol phthalin and 5 ml. of a 0.025 per cent. aqueous solution of copper sulphate. The solution of phenol phthalin is made by dissolving 0.5 gm. in 30 ml. of 90 per cent. alcohol, adding 20 gm. of sodium hydroxide and diluting the mixture to 150 ml. with air-free distilled water. If the distillate contains cyanide, the addition of the solutions of phenol phthalin and copper sulphate causes the development of a pink colour which is compared with that produced under similar conditions with standard solutions of cyanide. The test depends on the oxidation of phenol phthalin to phenol phthalein. Certain substances other than cyanide, for example hypochlorite, hypobromite, and hydrogen peroxide, also give a pink colour, but none of these substances was present in samples of water from the Estuary. The reaction is inhibited by sulphides, but if these are present in the sample they may be removed as lead sulphide by the addition of a solution of lead nitrate before distillation.

\* Supplied by the Laboratoire Hydrographique of the Conseil Permanent International pour l'Exploration de la Mer, Copenhagen.

According to Liebig's method, the sample is distilled into a small quantity of water containing 5 ml. of 5 per cent. aqueous solution of potash and a few drops of potassium iodide solution. The cyanide in the distillate is determined by titration with a standard solution of silver nitrate. On adding the silver nitrate, the silver cyanide first formed dissolves in the excess cyanide and titration is continued until a permanent opalescence results. If the distillate is placed in a test tube the point of permanent opalescence on addition of the silver nitrate can be conveniently observed by lateral illumination of the tube, which should be screened from other sources of light. The reaction between silver nitrate and cyanide is inhibited by the presence of sulphide, which should accordingly be removed by preliminary treatment with lead nitrate. Certain higher fatty acids volatile in steam also interfere with the reaction but these can be removed by preliminary precipitation with lime water.

In the method dependent on the conversion of cyanide to Prussian blue the sample is distilled and the cyanide in the distillate is determined colorimetrically by the blue colour produced in dilute solutions on the addition of ferrous sulphate, ferric chloride and hydrochloric acid. The reaction is specific for cyanides in the absence of soluble ferrocyanides.

The limiting concentrations of cyanide which can be estimated in Tees Estuary water by the three methods<sup>(8)</sup> just described are given in Table 116.

TABLE 116—*Sensitivity of Three Methods of Determination of Cyanide in Water from the Tees Estuary*

Method	Limit of detection	Limit for satisfactory estimation
	Gm. (CN) per 100 litres	Gm. (CN) per 100 litres
Phenol phthalin	0.0005	0.002
Silver nitrate	0.005	0.02
Prussian blue	0.2	0.4

The Prussian blue method was used for the determination of cyanide in coke oven effluents, but it was not sufficiently sensitive for use with Tees Estuary water, which did not usually contain more than 0.02 gm. (CN) per 100 litres. Throughout the investigation the phenol phthalin method was employed for samples of Estuary water and was checked by Liebig's method if the preliminary test showed cyanide equivalent to or exceeding 0.02 gm (CN) per 100 litres. Good agreement between the cyanide concentrations as determined by the two methods was obtained. Thus, in a series of 8 samples of Estuary water in which the cyanide as determined by silver nitrate varied from 0.013 to 0.207 gm. (CN) per 100 litres, the average difference between the values given by the two methods, expressed as a percentage of the higher value of each pair, was about 13. While both methods give fairly accurate values for the concentration of cyanide in the distillate from Estuary water, there is in both processes a considerable loss during the distillation. In a long series of experiments in which known amounts of cyanide were added to cyanide-free Estuary water and the cyanide was determined by analysis, it was found that an average of 90 to 95 per cent. of a concentration of 0.1 gm. (CN) per 100 litres was recovered, but at a concentration of 0.01 gm. (CN) per 100 litres the value given by analysis was only 45 to 55 per cent. of the true value.

## II. EFFECT OF ADDITION OF FORMALDEHYDE ON TOXICITY OF SOLUTIONS CONTAINING CYANIDE

Formaldehyde reacts with cyanide to form the cyanhydrin,  $\text{CH}_2(\text{OH})\text{CN}$ . The reaction is reversible<sup>(9)</sup> and to remove cyanide from dilute solutions a large excess of formaldehyde is necessary. Formaldehyde readily destroyed the toxicity of solutions of pure potassium cyanide in concentrations up to 1.0 gm. (CN) per 100 litres, the highest concentration examined; it had no effect on the toxicity of solutions of phenol or of *p*-cresol, nor on the toxicity of diluted spent still liquors which did not contain cyanides. In solutions containing mixtures of a phenolic substance and of cyanide, each present in a toxic concentration, the toxicity of the



solution after the addition of formaldehyde became equivalent to that of the phenolic substance alone.

Formaldehyde in relatively high concentrations is itself toxic to trout (Table 117).

TABLE 117—*Toxicity of Formaldehyde to Trout*

Approximate concentration of formaldehyde Gm. per 100 litres	Effect on Fish exposed for 10 hours	
	Dead	No. of Fish Alive
9.5 to 10	4	1
7.6 to 8	3	2
4.7 to 5	3	3
3.8 to 4	0	5

In the experiments reported in Chapter XIV, in which formaldehyde was added to samples of Estuary water, the quantity of formaldehyde was 2.9 gm. per 100 litres, a concentration below that toxic to trout.

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